Response to the comments of Anonymous Referee #2

Summary:

The oil sands (OS) in Alberta, Canada provide a significant source of SOA, necessitating lab studies to isolate contributions from different sources and chemical reactions. To address this knowledge gap, the authors use a custom oxidative flow reactor (OFR) to mimic different degrees of atmospheric oxidative aging for emissions from different OS-related precursors. In this work, the authors introduce the ECCC-OFR through single-species precursor experiments to assess the impacts of gas and particle wall losses and seeding, then use the ECCC-OFR to evaluate differences in OS-related SOA formation between several relevant sources. This is generally a clearly written manuscript, with compelling results that contribute important knowledge for both OS SOA chemistry as well as future OFR laboratory studies.

Response: We thank Anonymous Referee #2 for the review and the positive evaluation of our manuscript. We have fully considered the comments and made the associated revisions to our manuscript. The responses (blue text) and changes to the manuscript (red text) are listed below.

General Comments

[1] In the introduction (page 2, lines 22-24), the authors state that organic gases from the OS are mainly alkanes that react with the OH radical. However, one of the precursors that the authors use and discuss in the introduction is α-pinene. The choice of α-pinene is confusing in this context without further justification. From the manuscript, it seems that α-pinene was chosen because it was convenient to compare OFR operation to other studies. Does α-pinene have additional relevance for SOA in the OS region? Either way, it would be helpful for the author to address this choice early on in the manuscript. Additionally, under the ECCC-OFR operating conditions for these experiments (i.e., precursor concentrations, ozone concentrations), is there potential for the interfering α-pinene + ozone reaction to contribute significantly to SOA yields?

Response: According to our previous study (Liggio et al., 2016), α-pinene is likely the main SOA precursor for background OA in the OS region. We have added the following content in the revised manuscript for clarity (P3, L18-20): "Alkanes are the main component of OS emissions, while α-pinene is a representative biogenic precursor which likely contributes significantly to the background SOA observed in OS region (Liggio et al., 2016)."

We have also added "Under the operating conditions used here for α-pinene experiments, OH reaction contributes 64%-98% of the α-pinene gaseous loss across the entire OH exposure range, and >90% after 3 equivalent days, with α-pinene + O_3 reaction playing a minor role" in P8, L8-10 of the revised manuscript.

[2] Wall losses (Section 3.1.1): The authors state that vapor wall losses are likely minimal based on the diffusion timescale relative to the residence time within the reactor, then state the critical assumption that flow in the reactor is ideally laminar. Is this assumption solely based on fluid dynamics information from previously designed OFRs? The authors cite CFD done by Huang et al. (2017) for the CPOT on page 4 (lines 6-7) to justify the assumption, but I'm curious as to how the differences between the ECCC-OFR and the CPOT would change the fluid dynamics. For example, the ECCC-OFR has a straight outlet rather than a conical one like the CPOT. Is there potential for jetting or dead volume around the outlet? What are the benefits to sampling from the center line?

Response: We have now performed CFD simulations on the ECCC-OFR and included these results in the Supplement (Sect. S2).

To assess the near laminar flow of the ECCC-OFR, computational fluid dynamics (CFD) simulations were performed using ANSYS Fluent software (Version 2019 R2) in three dimensions to characterize the flow field inside the ECCC-OFR. Hybrid tetrahedral–hexahedral mesh consisting of 5.7 × 10^5 computation cells were used. Turbulence was modeled using a realizable k-epsilon model. The simulation results are shown in Fig. S4. It is shown in Fig. S4a that the flow velocity distribution in the reactor is generally uniform. A high velocity is observed only near the inlet, but reduces to the average velocity in the conical diffuser. The velocity distribution here indicates that jetting is much weaker in ECCC-OFR compared to PAM (Mitroo et al., 2018). Fig. S4b indicates that the flow field is quite good in ECCC-OFR, with a small recirculation zone, similar to previous studies using a conical diffusion inlet (Huang et al., 2017;Ihalainen et al., 2019), but much better than PAM (Mitroo et al., 2018).

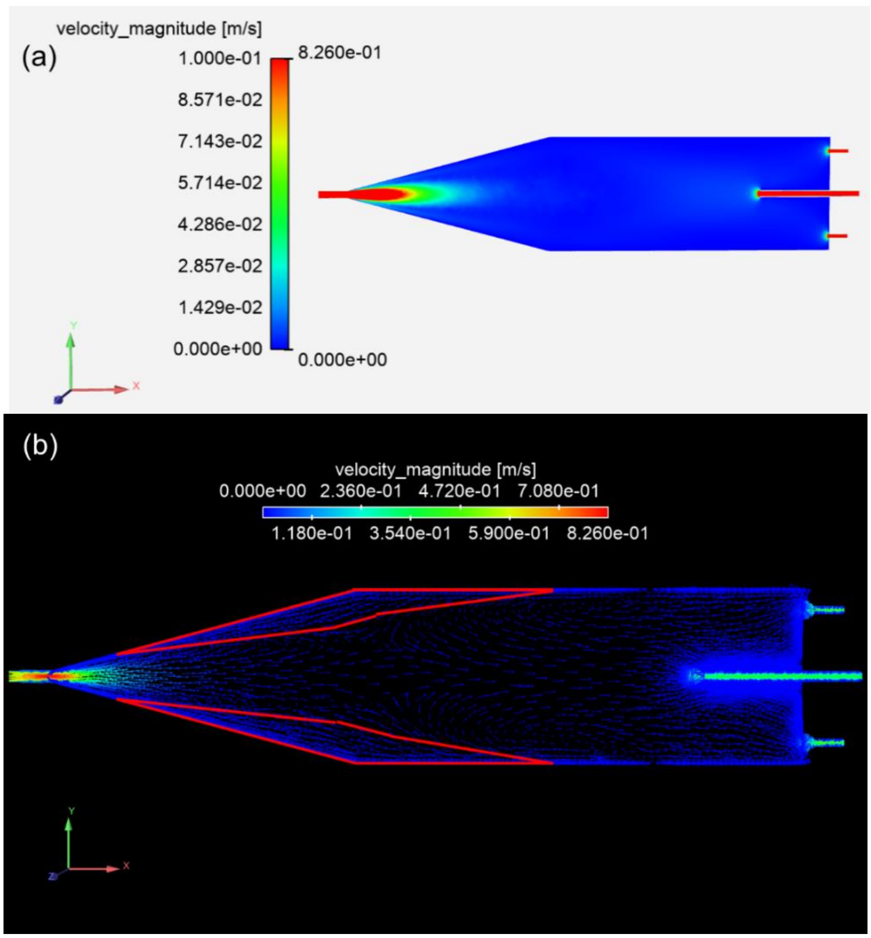

Figure S4. CFD simulation results: (a) velocity distribution; (b) vectors showing flow field. The red lines in (b) indicate the areas with recirculation.

Based upon the CFD simulation results above, we know that the flow field in ECCC-OFR is not perfectly ideal laminar flow, though it is significantly better than previous OFRs with a straight inlet, e.g., PAM (Mitroo et al., 2018). Hence, our assumption based on ideal laminar flow (using a diffusion timescale compared to the residence time to infer the gas-wall interactions) was removed in our revised paper (P7, L16-26).

From the CFD simulation results above, we also know that there is no jetting or dead volume around the sampling outlet. The non-laminar flow at the end of the OFR only influences the side flow, not the sampling flow.

The benefits to sampling from the centerline is the minimization of the interactions with walls (Lambe et al., 2011), as most of the flow that interacts with the walls exit from the side outlets.

Technical Comments

[1] Page 2, Lines 19-20: The authors state that a single species approach to studying SOA formation is "impractical." To me, "impractical" implies some sort of logistical difficulty and sells the point short. I'd consider reframing this sentence to emphasize atmospheric relevance for the OS, which is critical to consider when performing lab studies.

Response: We changed the sentence into "As a result, using a single species approach to studying SOA formation from OS is unrepresentative." (P2, L19-20).

[2] Page 2, Lines 21-22: Consider restructuring this sentence for clarity. Perhaps "Precursor emissions occur throughout the OS surface mining and processing production cycle, and they originate from sources including…"

Response: This sentence was modified to be "Precursor emissions occur throughout the OS surface mining and processing production cycle, and they originate from sources including open pit surface mines, processing plants and tailings ponds" (P2, L21-22).

[3] Page 2, Line 24: Define "OH" as "hydroxyl radicals (OH)" before using the abbreviation.

Response: Revised (P2, L24).

[4] Page 2, Line 28: "Complimentary" should be "complementary." This spelling should also be changed on page 3, line 13.

Response: Revised (P2, L28; P3, L13).

[5] Page 3, Line 6: Replace the semicolon after "vary" with a comma.

Response: Revised (P3, L6).

[6] Page 4, Line 11: Replace "Hg" with "mercury."

Response: Revised (P4, L12).

[7] Page 5, Line 5: Define the THC acronym here.

Response: Revised (P5, L17).

[8] Figure 1: Consider matching the color of the top and right axes to the alkane data points to visually distinguish the gas-phase data from the particle-phase data.

Response: The Figure 1 (now is Figure 2) is revised to be:

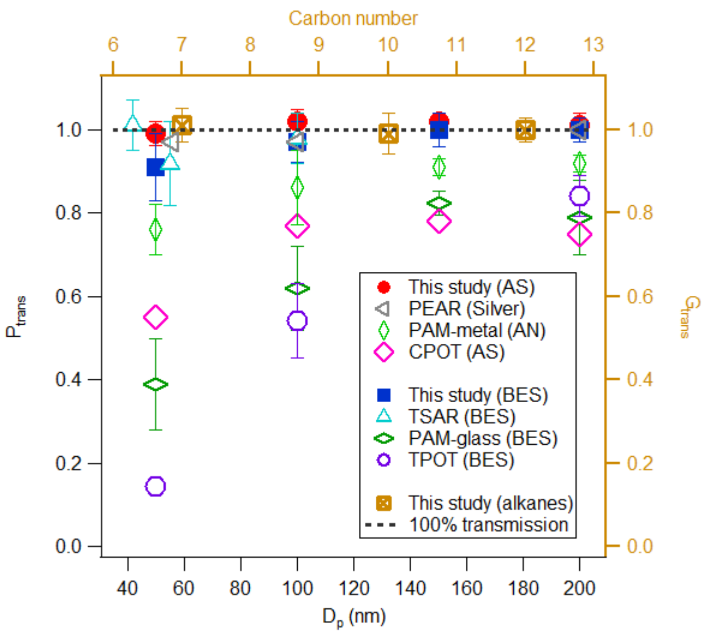

Figure 2. Particle (left and bottom axis) and gas (right and top axis) transmission efficiencies (P_{trans} and G_{trans}) for the ECCC-OFR. Particle transmission efficiencies of other OFRs are shown for comparison: PAM-glass and TPOT (Lambe et al., 2011), PAM-metal (Karjalainen et al., 2016), TSAR (Simonen et al., 2017), CPOT (Huang et al., 2017) and PEAR (Ihalainen et al., 2019).

[9] Page 8, line 9: The sentence starting with "This despite" is not a full sentence.

Response: This sentence was merged with previous sentence to be "…for unseeded experiments, despite initial concentrations of…" (P9, L5).

[10] Page 10, line 21: Replace the semicolon after "mixtures" with a comma.

Response: Revised (P11, L9).

[11] Page 10, line 25: It would be helpful to cite the specific section in supporting information so the reader can easily flip to it as needed.

Response: It was modified to be "… as described in detail in Sect. S5 of the Supplement" (P11. L13).

[12] Figure 4a and 4b: Consider emphasizing the different y axis scales between the two panels in either the text or the figure caption. Otherwise, the differences between seeded and non-seeded results can be difficult to pick out visually.

Response: "Note that the y-axis ranges are different in (a), (c), and (d)" was added in the figure caption (P24, L8).

[13] I would be interested to see the AMS mass spectra for each OS-related oxidation experiment, perhaps in the supplement.

Response: The AMS mass spectra for each OS-related oxidation experiment are shown in Figure S9. We have added "Although these precursors have very different SOA yields, their AMS mass spectra (Fig. S9) are similar, indicating a similar main precursor composition (alkanes)" at P11, L25-26 of the revised manuscript.

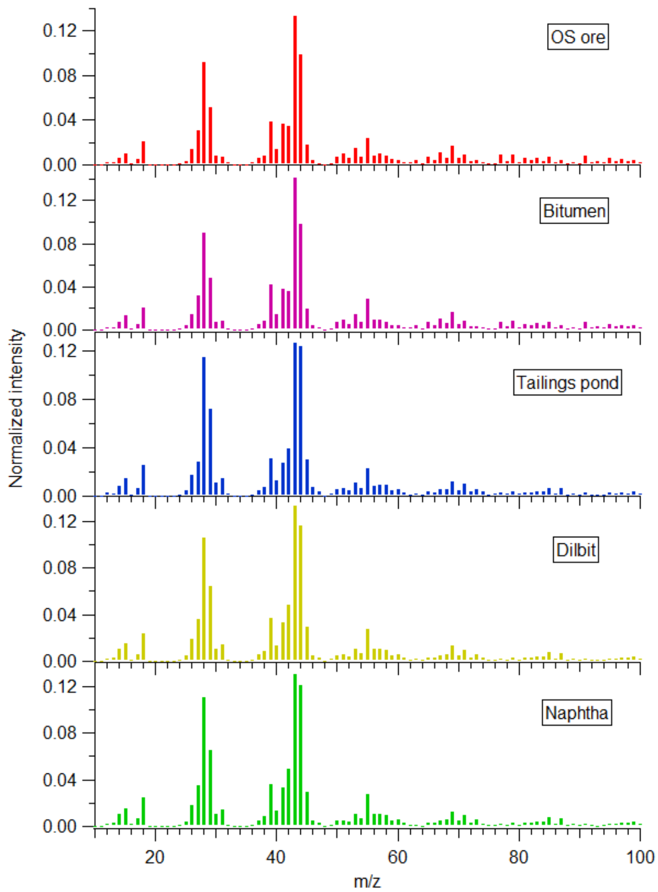

Figure S9. Representative AMS mass spectra for each OS-related oxidation experiment at OH exposure of ~1.5 × 10^{12} molec cm^{-3} s.

References

Huang, Y., Coggon, M. M., Zhao, R., Lignell, H., Bauer, M. U., Flagan, R. C., and Seinfeld, J. H.: The Caltech Photooxidation Flow Tube reactor: design, fluid dynamics and characterization, Atmospheric Measurement Techniques, 10, 839-867, 10.5194/amt-10-839-2017, 2017.

Ihalainen, M., Tiitta, P., Czech, H., Yli-Pirilä, P., Hartikainen, A., Kortelainen, M., Tissari, J., Stengel, B., Sklorz, M., Suhonen, H., Lamberg, H., Leskinen, A., Kiendler-Scharr, A., Harndorf, H., Zimmermann, R., Jokiniemi, J., and Sippula, O.: A novel high-volume Photochemical Emission

Aging flow tube Reactor (PEAR), Aerosol Science and Technology, 53, 276-294, 10.1080/02786826.2018.1559918, 2019.
Karjalainen, P., Timonen, H., Saukko, E., Kuuluvainen, H., Saarikoski, S., Aakko-Saksa, P., Murtonen, T., Bloss, M., Dal Maso, M., Simonen, P., Ahlberg, E., Svenningsson, B., Brune, W. H., Hillamo, R., Keskinen, J., and Rönkkö, T.: Time-resolved characterization of primary particle emissions and secondary particle formation from a modern gasoline passenger car, Atmospheric Chemistry and Physics, 16, 8559-8570, 10.5194/acp-16-8559-2016, 2016.
Lambe, A. T., Ahern, A. T., Williams, L. R., Slowik, J. G., Wong, J. P. S., Abbatt, J. P. D., Brune, W. H., Ng, N. L., Wright, J. P., Croasdale, D. R., Worsnop, D. R., Davidovits, P., and Onasch, T. B.: Characterization of aerosol photooxidation flow reactors: heterogeneous oxidation, secondary organic aerosol formation and cloud condensation nuclei activity measurements, Atmospheric Measurement Techniques, 4, 445-461, 10.5194/amt-4-445-2011, 2011.
Liggio, J., Li, S. M., Hayden, K., Taha, Y. M., Stroud, C., Darlington, A., Drollette, B. D., Gordon, M., Lee, P., Liu, P., Leithead, A., Moussa, S. G., Wang, D., O'Brien, J., Mittermeier, R. L., Brook, J. R., Lu, G., Staebler, R. M., Han, Y., Tokarek, T. W., Osthoff, H. D., Makar, P. A., Zhang, J., Plata, D. L., and Gentner, D. R.: Oil sands operations as a large source of secondary organic aerosols, Nature, 534, 91-94, 10.1038/nature17646, 2016.
Mitroo, D., Sun, Y., Combest, D. P., Kumar, P., and Williams, B. J.: Assessing the degree of plug flow in oxidation flow reactors (OFRs): a study on a potential aerosol mass (PAM) reactor, Atmospheric Measurement Techniques, 11, 1741-1756, 10.5194/amt-11-1741-2018, 2018.
Simonen, P., Saukko, E., Karjalainen, P., Timonen, H., Bloss, M., Aakko-Saksa, P., Rönkkö, T., Keskinen, J., and Dal Maso, M.: A new oxidation flow reactor for measuring secondary aerosol formation of rapidly changing emission sources, Atmospheric Measurement Techniques, 10, 1519-1537, 10.5194/amt-10-1519-2017, 2017.