

## ***Interactive comment on “Volatile organic emissions from the distillation and pyrolysis of vegetation” by J. P. Greenberg et al.***

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This is my first time reviewing for this journal. I am used to seeing the revised manuscript along with the detailed reply to my comments. Without actually seeing the revised manuscript it is hard to know if my concerns were well-understood. In particular, though it seems that I did not get some important points across. I reiterate them here in more detail, hopefully before the next draft gets too advanced, in case it will save time for all in the end

1) On the VOC/CO ratio for charcoal kiln emissions.

Both high-temperature and low temperature pyrolysis occur within a charcoal kiln. The

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CO/VOC ratio is higher for high temperature pyrolysis, because gasification reactions start at  $\sim 500$ – $600$  C that make CO and not VOC.

In any case, the best way to get the VOC/CO ratio for a charcoal kiln is thru measurements on an actual kiln. The second best way would be an experiment that probes both high and low temperature pyrolysis.

At least two studies report a VOC/CO ratio measured on actual charcoal kilns, but both have some shortcomings partially addresses by the manuscript under consideration here.

The first study is the one already quoted by Pennise et al., 2001. Some caveats about this study include:

The molar emission ratio for TNMHC to CO<sub>2</sub> in their Table 2 is on a per carbon basis and not a molar basis as claimed. The average number of carbons for a NMHC is unknown. They report high N<sub>2</sub>O emissions even though previous work had shown this is an artifact. Thus their technique may not be totally up to date. They used a metal sample inlet, which could cause loss of some species. They used a methaneizer to get TNMHC, which assumes a per carbon response proportional to methane, which in fact does not occur for some oxygenated organic compounds.

With these caveats in mind, Pennise et al., reported a gVOC/gCO ratio of 92.6/223, which equals .415 in their Table 6a. This ratio was based on the assumption that the NMOC had a per-carbon molecular weight of 18. This assumption could be questioned in light of the dominance of OVOC: I..E. the MW/C value for some common oxygenates is as follows:

HCOOH 46, CH<sub>3</sub>OH 32, HCHO 30, CH<sub>3</sub>COOH 30, acetone <20, phenol 15.7

So an argument could be made to use a number higher than 18 and adjust the VOC/CO ratio upwards. However it seems unlikely that a number close to 40 would be justified and that is what would be needed to get the VOC/CO ratio close to one as indicated in

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the current draft of the ms.

A second study that measured the VOC/CO ratio on an actual kiln was by Bertschi et al., 2003. Bertschi et al report a gVOC/gCO ratio of 0.339 in their Table 3. While they measured many VOC, their technique was certainly unable to measure all VOC. Thus the true ratio is higher.

The current ms gives a lot of insight into what the real gVOC/gCO value should be for two main reasons: 1) it measured a suite of VOC including some measured by Bertschi et al., and many that were not. Thus ratios to a common low temperature pyrolysis compound (such as methanol) could be used to derive a higher gVOC/gCO ratio than reported by Bertschi et al.. 2) The current ms also found that the identified VOC accounted for about 70% of the total mass of VOC. Based on this the gVOC/gCO can be adjusted even higher.

Using the two steps just above carefully would provide an improved estimate of charcoal kiln emissions on both a speciated and total basis!

2) On the flammability of the emissions The new information on the identity and amount of emissions is an important, highly-professional achievement. On the other hand, the flammability section strikes me as a back-of-the-envelope, rather informal digression in a journal that is not normally read by the combustion community anyway. Fire propagation is a complex topic with a developed scientific vocabulary and it involves temperatures much higher than those probed here. For instance, “sparks” is a technical term relevant to the breakdown of a gas above a threshold voltage. The things that look kind of like “sparks” in a biomass fire are actually “embers” - small glowing pieces of biomass that actually do play a huge role in fire propagation by being carried on the wind. To illustrate the second point, at the higher temperatures (1100C) biomass is exposed to in real fires, a larger fraction of the exposed solids can be gasified and at a higher rate! Also ignition of a small concentrated volume of gas can immediately ignite a large volume of gas below the flammability threshold. That is how a 2-chamber

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carburetor works. I guess I don't see how the current section makes a significant contribution to demystifying the complex topic of fire propagation, but of course, it's up to the authors to retain this if they want.

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