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

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Informal, Initial, Remarks by Robert J. Yokelson on: Volatile organic emissions from the distillation and pyrolysis of vegetation Author(s): J. Greenberg, H. Friedli, A. Guenther, D. Hanson, P. Harley, and T. Karl

General comment:

This is valuable work that provides measurements of atmospherically-important compounds generated by low-temperature heating of biomass. These compounds are also major emissions of biomass burning, especially charcoal production. The compounds reported include some for which only a little data is previously available. This

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manuscript (MS) has a few weaknesses, which can be easily taken care of by repackaging the presentation of the results. 1) MS does not refer to much relevant previous work on pyrolysis of biomass and one key paper on charcoal production. Citing this work and comparing with the previous results would improve the introduction and discussion. For instance, no reason is given why the experiments were terminated at 300C when fires routinely expose biomass to temperatures as high as 1100C. What little previous work has been done on fire and charcoal production emissions of some of the interesting compounds reported here is not cited. This MS could be repackaged as further evidence of the importance of these compounds - especially for charcoal kilns as will be explained in the detailed comments. I don't want to rewrite the paper myself, but just point the way to what I hope would be an enhanced product!! 2) The section on flammability of the emissions should be eliminated since any introductory combustion text makes two important points i) flames are the fast reaction of oxygen with a flammable gas, and ii) pyrolysis of the solid fuel is the source of the flammable gas mixture that feeds the flames in solid-fuel combustion. Basically, flaming combustion of solid fuel is impossible if the pyrolysis does not generate a flammable mixture. Also, a simple experiment shows that heating biomass produces a flammable mixture. Place a chunk of biomass on a hotplate. In a few moments a white smoke is generated, which can easily be ignited. 3) Acetic acid appears at the same mass as glycolaldehyde, which can be the main product of heating biomass. Thus the results reported as "acetic acid" should be consistently flagged as a possible mixture. Ditto for furan, which shares a mass with isoprene.

Specific comments: Abstract line 5 and 6 Acetic acid and furan should be presented with caveats since those masses can represent at least two compounds emitted by heated biomass. See:

Christian, T.J., B. Kleiss, R.J. Yokelson, R. Holzinger, P.J. Crutzen, W.M. Hao, T. Shirai, and D.R. Blake, Comprehensive laboratory measurements of biomass-burning emissions: 2, First intercomparison of open path FTIR, PTR-MS, GC-MS/FID/ECD, J. Geophys. Res., 109, D02311, doi:10.1029/2003JD003874, 2004.

Abstract lines 13-16 I would eliminate the flammability stuff from the paper as explained above.

Abstract last two sentences FTIR-based field measurements of charcoal kiln emissions quantified some of the compounds also detected here from heated biomass. I recommend these authors piggy-back off the FTIR-based field measurements to get reasonable, but qualified estimates of charcoal kiln emissions for some compounds that could not be detected by FTIR (vide infra). Revised abstract could reflect this. The paper I refer to is:

Bertschi, I.T., R.J. Yokelson, D.E. Ward, T.J. Christian, and W.M. Hao, Trace gas emissions from the production and use of domestic biofuels in Zambia measured by open-path Fourier transform infrared spectroscopy, J. Geophys. Res., 108, 8469, doi:10.1029/2002JD002158, 2003.

Intro, line (L) 1 Minor point, biomass combustion occurs in stages mostly in gedanken experiments. In real life it “involves many simultaneous processes,” which includes gasification (commonly known as glowing combustion).

Intro L7 The Andreae and Merlet review is now quite out of date and more complete tabulations of fire emissions are given in: Christian, T. J., B. Kleiss, R. J. Yokelson, R. Holzinger, P. J. Crutzen, W. M. Hao, B. H. Saharjo, and D. E. Ward, Comprehensive laboratory measurements of biomass-burning emissions: 1. Emissions from Indonesian, African, and other fuels, J. Geophys. Res., 108, 4719, doi:10.1029/2003JD003704, 2003. In particular, this paper gives values for fire emissions of some of the species these authors detected - using the same instrumentation. Worth comparing too in results and discussion! (Section 4.5)

Experimental section 2. General comments: This is a classic TG-EGA experiment carried out in N2 and air and the description is not bad. However, well over 1000 papers in the literature describe remarkably similar experiments and nearly all of them extended their temperature program to temperatures well above 300C to capture the peak of low-temperature pyrolysis (LTP) near 350C and the emissions from high temperature pyrolysis (HTP) at temps of 400-600C. The authors should refer to some of the previous work and mention the fact that these experiments probed only a large part of the low-temperature regime. I think later in the discussion they can argue that they probed a large enough fraction of the low-temperature regime to get meaningful data for low-T emissions. TG_EGA using FTIR as the detection method for biomass pyrolysis compounds such as methanol, acetic acid, etcĚis common see: Lephardt, J. O., and R. A. Fenner, Characterization of pyrolysis and combustion of complex systems using Fourier transform infrared spectroscopy, Appl Spectrosc., 34, 174-185, 1980. Fenner, R. A. and J. O. Lephardt, Examination of the thermal decomposition of Kraft pine lignin by Fourier transform infrared evolved gas analysis, J. Agric. Food Chem., 29, 846-849, 1981. DeGroot, W. F., W. Pan, M. D. Rahman, and G. N. Richards, First chemical events in pyrolysis of wood, J. Anal. Appl. Pyrolysis, 13, 221-231, 1988. Djilas, S. M., B. L. Milic, and P. I. Premovic, Pyrolysis evolved gas Fourier transform infrared spectroscopy analysis of aminobutanoic acid isomers, J. Anal Appl. Pyrolysis, 29, 103-110, 1994.

Some really nice previous work using mass-spec for on-line analysis of pyrolysis products from biomass includes: Evans, R. J., T. A. Milne, and M. N. Soltys, Direct mass-spectrometric studies of the pyrolysis of carbonaceous fuels, III, Primary pyrolysis of lignin, J. Anal. Appl. Pyrolysis, 9, 207-236, 1986. Evans, R. J. and T. A. Milne, Molecular characterization of the pyrolysis of biomass. 1. Fundamentals, Energy and Fuels, 1, 123-137, 1987.

Collections of nice pyrolysis TG-EGA papers occur in books such as the following: Shafizadeh, F., and W. F. DeGroot, Combustion characteristics of cellulosic fuels, in Thermal Uses and Properties of Carbohydrates and Lignins, edited by F. Shafizadeh, K. V. Sarkanen, and D. A. Tillman, pp. 1-18, Academic, San Diego, Calif., 1976. Overend, R.P., T.A. Milne, and L.K. Mudge, Fundamentals of thermochemical biomass conversion, Elsevier, 1985.

I tried to summarize the huge body of work on biomass pyrolysis in several of my papers. With the assistance of Geoff Richards who published over 200 papers on biomass pyrolysis, I developed a figure showing high and low T biomass pyrolysis products. See Figure 7 of: Yokelson, R.J., D.W.T. Griffith, and D.E. Ward, Open-path Fourier transform infrared studies of large-scale laboratory biomass fires, J. Geophys. Res., 101, 21067-21080, 1996. and Yokelson, R.J., D.E. Ward, R.A. Susott, J. Reardon, and D.W.T. Griffith, Emissions from smoldering combustion of biomass measured by open-path Fourier transform infrared spectroscopy, J. Geophys. Res., 102, 18865-18877, 1997.

There are also issues having to do with compound identification not fully addressed in the MS. For instance glycolaldehyde (mass 60) is the main product generated by fast heating of natural cellulose. Only by acid washing cellulose can the glycolaldehyde production be suppressed. See: Richards, G. N., Glycolaldehyde from pyrolysis of cellulose, J. Anal. Appl. Pyrolysis, 10, 251-255, 1987.

Radlein, D., J. Piskorz, and D. S. Scott, Fast pyrolysis of natural polysaccharides as a potential industrial process, J. Anal. Appl. Pyrolysis, 19, 41-63, 1991.

Thamburaj, R., Fast Pyrolysis of Biomass for Green Power Generation, presented at 1st World Conference on Biomass for Energy and Industry, Seville, Spain, 2000.

Finally many studies of low-T biomass pyrolysis detected ethylene and formic acid as major products. The ethylene would presumably be detected by GC-MS?

A non-experimental minor point: Section 2.2 last sentence of paragraph 1: Sugar cane is burned before the harvest to make harvest easier!

Results section 3 3.1 GCMS line 6: ethylene not detected?

Section 3.3 last sentence: CO and CO2 are suppressed at high T in N2, because chemisorption of O2 is exothermic and is needed to promote gasification. See Figure 7 of Yokelson et al 1996 or one of the original references such as: Hshieh, F. Y., and G. N. Richards, Factors influencing chemisorption and ignition of wood chars, Combust. Flame, 76, 37-47, 1989.

Discussion Section 4 General comments: Just a heads up, which may not need to be in the authors' paper. The biomass was fairly wet in these experiments, which has an influence on the pyrolysis chemistry as an examination of the literature will show.

In addition to CO and CO2, alkanes and aromatics are evolved by biomass pyrolysis between 400 and 600C.

Bertschi et al reviewed typical charcoal carbon contents.

Charcoal kiln biomass temperatures get into the high-temperature regime, thus this work is most relevant for compounds produced by low-T pyrolysis.

Yokelson et al., 1996 measured the emissions from pyrolysis alone, but did not report them. The measurements quoted in Table 3 of the MS were for a mixture of pyrolysis and mostly flaming and thus not directly comparable.

The authors TG curves show a max near 350C and indicate termination of low-T pyrolysis generation near 400C. This is in agreement with countless previous papers. Thus, measurements up to 300C probably gave "reasonably representative" data of the whole low-T process.

Specific comments: 4 lines up from section 4.3 header. VOC emissions were about 1/3 of the CO2 emissions and not the major weight fraction according to the abstract? Section 4.3 last sentence: The terpene/pyrazine could be higher for leaves than wood, because leaves have higher nitrogen and leaves such as Eucalyptus can be up to 10% volatiles. Cellulose does not contain nitrogen so I don't think cellulose pyrolysis should be given as a pyrazine source. Section 4.5 last paragraph is good place to compare to Christian et al., 2003

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Section 4.6 currently has no real point that I can see. However, I would expand this section as follows: Table 3 of Bertschi et al biofuels paper shows NMOC/CO emission ratio as .234 rather than close to 1 (as indicated by Table 2 of this work). This is because high-T pyrolysis occurs in charcoal kilns driven by gasification - the heat source in a kiln. Bertschi and the authors of this MS both report the following low-T pyrolysis compounds: methanol, phenol, furan, and acetic acid (with some caveats). However, the current work gives data for several low-T compounds not readily measured by the FTIR technique employed by Bertshci et al: butadiene, acetaldehyde, acetone, methyl acetate. By using the compounds measured by both groups as a sort of “internal standard” the current work could yield estimates for some new compounds. I would use the oak wood data as that most relevant to tropical charcoal production. This I see as the main value of this work.

Figure 3 Middle graph says it is acetaldehyde while figure caption refers to acetone. Also, the butadione emissions are surprisingly high! Bigger than methanol! I don’t think it happens for fires, but may for pure leaf pyrolysis.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 9097, 2005.