

Interactive comment on “Water vapor release from biofuel combustion” by R. S. Parmar et al.

R. Yokelson (Referee)

bob.yokelson@umontana.edu

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Referee comments on acpd-2008-0048

By Robert J. Yokelson

As it stands this paper mostly summarizes some obvious chemistry and does not make a large new scientific contribution. There may also be errors in the interpretation of the data. If it can be shown that the author's analysis of the data is meaningful, then some more rigorous analysis/discussion should be added to the paper to make it more worthwhile to publish.

Our group has been doing similar work as an intrinsic, but unpublished part of our fire research. I summarize that work to help clarify my views of this manuscript.

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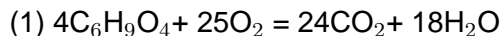
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Part 1: General comments on experimental procedure.

Beginning with the obvious, one can react an approximate formula for biomass with O_2 to make CO_2 and H_2O as follows:



This yields water as a combustion product at 75% of CO_2 . Allowing for some CO production, one can write (e.g.):



In this case, the H_2O/CO_2 ratio goes to 90%, but the ratio of $H_2O/(CO_2+CO)$ is still 75%. It is not explicitly shown by the authors, but one can also allow for some “typical” hydrocarbon production as follows (e.g.):



In this case the $H_2O/(CO_2+CO+CH_4)$ is about 71%

So in general it's a decent approximation to assume that the water made by combustion of the biomass or “combustion water” (CW) can be expressed as a function of the H:C ratio in the biomass and the carbon produced in the combustion reaction (C_c) as follows:

$$(4) CW = (H:C/2) * C_c$$

There is also unbound water in biomass, both in living plants and in long-dead biomass mostly as a result of exposure to the environment. This water is commonly termed “fuel moisture” (FM). As the FM evaporates during a laboratory fire it must be equal to:

$$(5) FM = \text{total water in plume} - \text{background water} - CW.$$

So far all I have said is in agreement with the authors. Next I show an excerpt from typical data we obtain. In this 1989 example (Figure 1, <https://www.umd.edu/chemistry/faculty/yokelson/misc/Figure1-acpd-8-4483-2008.pdf>

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) the excess C_c is approximated as $CO_2+CO+CH_4$ and the ratio of CW to C_c is approximated as 0.75. In the fire shown, freshly-cut sagebrush plants were ignited and a flame front passed across the fuel bed followed by a smoldering-only phase and finally extinction.

Note that in this case the fuel moisture evolution appears to go negative after the flame front is gone. This is an artifact due to the approximations involved, which include:

1. The real H:C ratio in the fuel is probably not exactly 1.5 and the CW to C_c ratio may also not be exactly 0.75. Also, the H:C ratio of the fuel may decrease over the course of the fire due to charring of the fuel.
2. Once the flames are far enough away, or out, areas can cool and reabsorb water. One actually sees an increase in the fuel bed mass at the very end of an experiment due to this.

In the following type of experiment, we can estimate the fuel moisture percentage (on a dry weight basis) by comparing the integrated mass of fuel moisture evaporated to the integrated mass of carbon volatilized divided by the mass fraction of C in the fuel F_C .

$$(6) \text{ FM\% (dry basis) } = 100 * \text{FM}_{\text{tot}} / \text{C}_{\text{tot}} / F_C$$

For the freshly cut sagebrush twigs and foliage (in the above example) the average fuel moisture of the whole fuel complex was estimated to be $50 \pm 5\%$. This is useful because subsampling a mixed fuel to measure the FM by weight loss is challenging. It is also possible to do the following. The mass loss record for the fuel bed can be adjusted for the amount of fuel moisture evaporated in real time to get a carbon mass loss versus time. We find that the carbon mass loss agrees well with carbon flux in the emissions – a useful check. Finally, we can (and frequently do) burn 100% pure ethanol, which has no fuel moisture, a known F_C and H:C ratio, and produces nearly all CO_2 and water to check our hot-wire flow meter calibration against our scales.

With homogeneous biomass fuels we can also estimate the fuel moisture by weighing

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till dryness and using:

$$(7) \text{ FM\% (dry basis) } = 100 * ((\text{wet weight} - \text{dry weight}) / \text{dry weight})$$

And we can also measure the H:C ratio of the biomass fuel subsample and use that ratio in our CW calculation. The FM percentages obtained this way are generally within $\pm 20\%$ of the value obtained by measuring the fuel moisture evolution (equations 4-6). Some additional uncertainties that effect this particular comparison include how well the subsample reflects the fuel moisture, the F_C , and the H:C of the bulk fuel; and the fact that there is often some residual fuel that was dried, but not burned.

In light of the above, the author's experiments have some features that worry me.

1. The ignition method is not described. They could be boiling off fuel moisture or absorbed water on surfaces (while volatilizing very little biomass carbon) during ignition, but not including this in the analyzed part of the data. Indeed the figures tend to show a spike in H_2O near the beginning of each fire. An intense ignition method could also make it possible to burn fuels that might not burn under many circumstances in nature (vide infra).

2. They reload fuel during the experiment, which could introduce a heat sink. In nature, the fuel is preheated and to some extent dried by an advancing fire before ignition.

3. The most important issue is that the data sets shown in their figures tend to end with the carbon emissions still at their peak values. This suggests that the data is not fire-integrated as the authors claim. The significance is that data is collected while fuel moisture is being boiled off, but not until all the carbon production is complete. This does not necessarily invalidate the data for all purposes, but would cause an overestimate of the bulk fuel moisture.

Part 2: General comments on uses of this type of data

The satisfactory agreement we obtained when comparing bulk fuel moistures estimated from smoke water measurements to the results from weighing/drying got us

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interested in several potential applications of smoke water measurements. One was the possibility that the fuel moisture of fuels burning in the wild could be roughly estimated from equations 4 - 6. This is useful in part because the fuel moisture of the fuel complex on a large-scale wildland fire can be hard to measure, but the H:C ratio can be assumed to fall within a fairly narrow range. However, this turned out to be more difficult than we anticipated. While the experiment is easy in the lab, it is more difficult in the field in real smoke plumes 200-1000 meters above ground level. This is primarily because our grab sample data for water reflects the high variability in the background water concentration. This then leads to excessive noise or variability in the computed excess water in the plume. In some cases, the plume even appears drier than nearby background air! See more on this at the end of part 2. We may revisit this problem some day using continuous airborne water data. Also, initially intriguing was the possibility that the fuel moisture (FM) impacts the amount and/or rate of fuel consumption and/or the relative amount of flaming and smoldering combustion in both the lab and the field. Thus, we also planned to compare the fuel moisture measured either directly (or by eqn's 4-6) to the CO/CO₂ ratio, which serves as an index of the smoldering to flaming ratio. For instance a positive correlation between FM and CO/CO₂ ratio could indicate that high fuel moistures promoted smoldering combustion. We never actually had time to carry this out. We also assumed that the water added to the atmosphere by fires would be insignificant compared to the water already present and did not publish any of this type of data as noted above. Thus, some questions we had then remain. Does FM impact the flaming to smoldering ratio or the total amount or rate of fuel consumption? By extension then, does FM impact the emission chemistry and/or heat release and plume dynamics?

More recently, interest has increased in other phenomena that may be affected by the water concentration in a smoke plume. Examples of this include: (1) the rapid initial photochemistry in the plume, (2) the formation of pyrocumulus clouds, and (3) the formation of "superfog," a combination of smoke and fog that tends to occur at night on prescribed fires in the southeastern US and has caused many fatal traffic accidents.

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My main criticism of the paper, assuming that my concerns about the data can be addressed, is that it mostly states the obvious basic chemistry and does not yield new insight into the impact of the water in the plume. Thus, I make some suggestions for the authors to expand their analysis in that respect.

1. The authors have CO and CO₂ data, so they could check for a correlation between FM (if their FM data is OK) and CO/CO₂.
2. The authors have carbon-flux data and may be able to determine if FM affects the carbon-flux rate and thus the heat release rate. (The heat of combustion for various wildland fuels has been measured: Susott, R.A., Characterization of the thermal properties of forest fuels by combustible gas analysis, Forest Sci., 28, 404-420, 1982.)
3. The effect of a change in water concentration on the first hour or so of chemistry in a smoke plume could be investigated with a box model.
4. The effect that FM might have on the formation of superfog could possibly be further investigated. Superfog is likely simpler to investigate than pyrocumulus clouds as it is a ground-level phenomenon. A good place to start would be to investigate the work of Gary Achtemeier and/or contact him directly. Dr Achtemeier believes that the water needed to form superfog comes from combustion of the biomass and has published this according to the emails from him that I show next (I added the italics):

Email on Jan 9, 2008:

The last of 3 peer reviewed papers on "superfog" and how it forms should go to a journal by the end of this month. This is the fourth fatal accident caused by smoke/fog in the South so far this burn season.

Gary L. Achtemeier, Ph.D USDA Forest Service 320 Green Street, Athens, GA 30602
Ph: 706-559-4239 FAX: 706-559-4317

email: gachtemeier@fs.fed.us

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and follow up email on Jan 14, 2008:

Bob.... Last fall I got the second of three papers on fog/smoke – superfog accepted for publication in Journal of Applied Meteorology. This paper explains how superfog forms. Third paper is in internal review and I hope to get it out by the end of this month. This paper deals with actual measurements of superfog I generated from burning forest litter. Visibility was 10 cm. There is some stuff in the literature about 30 years ago about number of PM particles released in smoke from a gram of wood consumed. So if you have the instruments, it might be good to get some new measurements.

Furthermore, the moisture for the superdense fog comes from water released during combustion. So we need measurements of liquid water/vapor water in smoke. Collaboration on smoke/particle/water would be appreciated.

Gary L. Achtemeier, Ph.D

5. The potential impact of FM on pyrocumulus formation could be treated more rigorously. In my experience, pyrocumulus most often form when a smoke plume has the energy to penetrate the top of the boundary layer and suddenly enter the relatively dry/cold free troposphere. The occurrence of these events should be strongly impacted by the heat release by both the fire and condensation and by wind speed. Thus, if FM acts as a heat sink (as the authors mention) it could have both a positive and negative influence on pyrocumulus formation. A detailed dynamic model would likely be needed to rigorously progress on this question (E.G. Latham, D. J., Plump: a plume predictor and cloud model for fire managers, U.S. Dept. of Agriculture, Forest Service, Intermountain Research Station General technical report INT; 314, pp.15, Ogden, UT, 1994). However, even if the authors do not use the output of a detailed model in this work, their speculation should be more specific as to the factors, trade-offs, feedbacks involved. The current analysis is too simplistic. Note several things in parts A) and B) of Figure 2, <https://www.umd.edu/chemistry/faculty/yokelson/misc/Figure2-acpd-8-4483-2008.pdf>) showing the water mixing ratio in ambient air

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and a smoke plume (with no pyrocumulus cloud) in Brazil. (1) Due to background variability, there is no significant difference between plume and background water absolute mixing ratio, (2) In light of (1), the fuel moisture and combustion water are not making extraordinary contributions to the plume water content, and (3) despite the very high water content, no pyrocumulus cloud formed. In contrast, part c) shows the data from a plume in Africa where a pyrocumulus cloud did form (see picture in Figure 2). Note that (1) the plume and background water mixing ratios are still similar in the boundary layer, (2) the plume water content is much lower, and (3) the cloud formed at the point where the plume penetrated to the free troposphere (level indicated by the very low background water value at ~ 13 km).

Part 3: Other specific comments in order of their location in this draft.

Title/Short Title/throughout text:

The term “biomass” is preferred to “biofuel” since the latter usually denotes biomass that is used as a household energy source.

Abstract Line 9 and throughout the text and tables:

Normally 15-40% fuel moisture (on a dry weight basis) is considered the “moisture of extinction” above which dead fuels will not sustain flaming combustion (<http://www.wrh.noaa.gov/sew/fire/olm/fuelmoisture.htm>). The extinction values are usually below 30 % (<http://www.fs.fed.us/land/wfas/firepot/fpipap.htm>). However, in the authors work 33% was the lowest fuel moisture obtained. This causes me to suspect there is an error in their FM determination (most likely the fact that the fires were not “completed” as explained above). We find that fuels stored indoors typically have fuel moistures ranging from 5-10%. The author’s speculate that the traditional method of estimating biomass fuel moisture (drying until constant weight) could cause large overestimates due to internal water that can only escape when the fuel structure is destroyed. This is not apriori impossible and it is required by the laws of thermodynamics that heating/drying biomass until weight

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is constant leaves some water on/in the biomass. However, experiments done here find good agreement between fire-integrated smoke water and weight-based FM determinations. Also, work done here drying fuels shows that the constant final weight persists for weeks using ovens, microwaves, grinding, etc. Thus, I suspect that the weight-based determinations may be accurate to within a few percent. Therefore, a suggestion to the contrary should ideally be supported by straightforward, simultaneous measurements made by both techniques. Finally, it is of course easy to burn fuels in the lab that are beyond the moisture of extinction if you use an aggressive ignition technique that dries out a large enough portion of the fuel.

Page (P) 4485, Line (L) 11-12

Here the author's simply state that dead fuels normally have a moisture up to 10% as if there is no controversy about the weight-based methods.

Page (P) 4486, Line (L) 3

The H:C/2 fixes the H₂O/CO₂ ratio from complete combustion so no calculation is needed.

Also either here, or somewhere before here, the authors need to mention the concept of excess concentrations above background and define the “del” notation, which is introduced later in this paper without explanation. Then the word “excess” or the symbol for excess (capital greek letter delta) should go before the word “water” and also probably before both H₂O and CO₂. That is because the background water and carbon need to be subtracted to analyze the smoke data.

P4486, L10-13

Too little detail, no specifics on why rejected or should not be neglected.

P 4486, L 13-14

There is no question here. Obviously if water is measured it tells you how much water

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is in smoke. I would just say you measured the water concentration in smoke.

P4486, L25

Should “container” be “chamber” for consistency?

P4487, L4

Standard 20 foot container = ?; the units are not metric or volumetric.

P4487, L5

Do the words “another one” indicate the fuel burning chamber? If so, maybe just say that? Maybe a diagram is needed as reviewer 3 mentions.

P4487, L7

How much moisture could have been lost from the fuel during the ignition process and how much could have been liberated from the walls early in each fire? For instance, Figure 1 shows a prominent water spike at the beginning. We never saw that. How was fuel ignited? We usually use a match (minimal influence), but did they perhaps use a propane torch (heat and carbon) and for how long? Or did they use an electrically heated igniter (heat only)?

P4487, L28-29

Was a door opened to reload fuel? How much fuel was reloaded? It seems like this would act as a heat sink and also cause a temporary dip in emissions production that I may see in the figures. Not sure this mimics real fires where heat radiated from the fire can pre-dry the fuel before the flames impinge on it.

P 4488, L 7

Here the excess notation is used without prior definition as noted earlier.

P4488, L11-27

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These are somewhat non traditional lab fire trajectories compared e.g. to published work by us or Lobert et al. In light of my earlier comments about these fires, I think the authors may need to re-think their interpretation – at least regarding fuel moisture determination.

P4489, L1-2

“combined” should be “presented”?

P4489, L9-10

A value larger than 0.75 (not 1.0) suggests a contribution of FM and is expected since a perfectly dry fuel is impossible.

P4489, L15

The words “must be” should be changed to reflect that this is an estimate.

P4490, L3

Yes live fuels have higher moisture. The authors should quote some work on the relative consumption of live and dead fuels to strengthen their case.

P4490, L5

The authors seem to misunderstand the nature of sugar cane fires. The farmers do not burn the live sugar cane plants, which would be a disaster for them. The fires are set to remove accumulated dead biomass, weeds, and animal and insect pests before cutting the live cane. After exposure to the high temperatures of the fire, the live plants deteriorate rapidly and must be pressed at the mill within ~ 24 hours. For this reason, the burns are usually scheduled in early morning to allow time for subsequent harvest and loading/transport during daylight. Additional reasons to burn in the morning are that the lower wind speeds reduce both the chances of the fire escaping the desired perimeter and the smoke impacts on local populations. It follows that burning in the morning with lower wind speeds and a lower boundary layer increases the chances

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of the plume penetrating to the free troposphere and forming a pyrocumulus cloud. Finally, the ambient humidity is typically higher in AM.

P4490, L15

A little confusing because all combustion would disrupt the structure of biomass.

P4490, L17-19

It seems like some simple experiments to test this should be feasible to add to this work?

P4491, L14-17

The author's fuel moisture values may not be accurate as mentioned above. In any case, the value of 40% should be investigated by using a range of live and dead moistures and some estimate of the relative proportion of these fuel types that burn. E.G. If the dead fuels were at 10% and the live fuels at 200% and a crown fire consumed about equal amounts of each then Trentmann's estimate of 40% might be low. But if the live fuels were at 80% then it would be very close. So at this point, the authors should probe this question with some real literature values rather than just speculating.

P4491, L21-23

We (and probably others) have massive amounts of smoke water data, but as mentioned above, the interpretation is not simple. Long before the plume has evolved to the point where a cloud might form it has diluted enough so that the water enhancements in the boundary layer plume are small compared to the water variability in the background air.

Table 1

It is interesting that the fuel with the highest FM "pine with green" also had one of the lowest fuel moistures in another run. Also the "dry run" of "pine with green" had a higher minimum H_2O/C ratio than the "wet" run of the same fuel.

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Summary. The authors need to rigorously determine which results are valid and then add some detailed, new scientific analysis to make this paper useful. Stated another way, a few key issues in point . . . response format are:

1. Smoke has water from evaporated fuel moisture in it . . . that's obvious.
2. The smoke water content was measured . . . good, but more needs to be said about how representative the fuels and measurements were.
3. The smoke water could have importance . . . yes, but shed some new, quantitative light on this to make the paper a valuable addition to the literature.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 4483, 2008.

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