Representative sampling in biomass studies—not so fast!

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Proper execution of representative sampling and laboratory mass reduction procedures are critical for the validity and reliability of chemical analyses of highly heterogeneous biomass fuels. In the study reported by Thy et al.,[1] it was demonstrated that faulty sampling had resulted in apparent ash compositions that differed from the true compositions by factors of two to three for many major oxides. Analytical results based on non-representative samples may thus not be representative for the specific fuel and processes being studied. Despite the general acceptance that accurate and representative compositions is a critical prerequisite for understanding reactions and elemental fractionation, the biomass energy community appears largely to have ignored the critical issues surrounding representative primary sampling. This can have resulted in misleading or faulty conclusions and may have restricted reliable predictive modelling.

Background

Knowledge of representative compositions of biomass fuels and their derivatives is critical for understanding reactions and elemental fractionation during thermal conversion such as fuel combustion. Achieving proper knowledge for highly heterogeneous biomass fuels is not a straightforward matter, but calls for careful considerations of the primary sampling procedures. Although the literature outside the biomass realm contains a wealth of established sampling principles, drying and ashing used as mass-reduction measures in fuel and combustion studies introduce further complexities. This mandates careful considerations also of laboratory procedures such as mass reduction techniques for secondary sampling of biomass byproducts in addition to the analytical procedures themselves. Despite the general knowledge in other fields that sampling errors can attain magnitudes of 20–50 times the analytical errors alone, in biomass studies the focus is all too often mainly on the precision of the analytical procedures alone, which is usually gauged by repeating the analytical procedure. Thus the quality of chemical analysis is typically evaluated by analysing as unknowns, well-characterised and compositionally similar standards. This approach only furthers the total analytical uncertainty for controlled samples, however (certified standards or in-house standards). But highly precise chemical analyses are of very limited blessing if the materials analysed are based on faulty or poorly documented and little understood sampling and mass reduction procedures. The main guarantee for accuracy of the analytical results rests with the documented representativeness of the entire sampling pathway.[2]

The biomass and energy community has unfortunately largely ignored or underestimated the effects of these problems. This can have impeded the ability to perform accurate predictive modelling, either experimentally or theoretically, of phase equilibria, elemental mobility and fractionation, and physical behaviour of residual silicate systems from thermal conversion of biomass materials.

This short note refers to a case study of the possible detrimental effect of non-representative chemical analyses on predicting relative element mobility during combustion of common wood fuel published by Thy et al.[1]

Wood fuel case story

This study reported attempts to characterise the inorganic part of a mixed conifer wood (mixed white fir and ponderosa pine), which was obtained from an operating power plant in California. The average grain-size of the fuel chips was inch-size (2–3 cm) and composed principally of solid wood with only minor bark, branches and foliage (Figure 1). The fuel was treated using standard methods of drying. The total air-dried mass of about 150 kg was stored in a closed master bin.

Three samples were taken from the master bin over the years of the duration of the study, two 1 kg primary samples (from which were produced 100 g of ashes for each). The analytical results in the present studies were elemental analyses of the ash fraction. These two samples were analysed twice by the same established commercial laboratory following accepted ASTM standard protocols. A larger primary fuel sample (25 kg) was also

extracted from the same bin, which was milled to a finer 3-mm grain-size before being ashed in a similar fashion. This latter ash (~2500 g) was sampled after manual homogenisation, the analytical mass was 3 g and analysed by X-ray fluorescence techniques. The same ash was similarly sampled and analysed by the earlier used commercial laboratory mentioned following the same ASTM standard protocols previously used. Thus there is a basis for comparison of the analytical results based on this small experimental sampling design.

The four analyses summarised in Table 1 were all obtained with the purpose of representing the ash fraction of the same wood fuel. Since the particular purpose of the study was to evaluate alkali metal volatilisation as a function of temperature, see Reference 1 for details, an accurate knowledge of the ash composition was critical. NIST fly ash reference material was analysed concurrently with the unknown wood ashes and the results are also listed in Table 1 together with their recommended standard values.

Comparison of the results in Table 1 reveals very large discrepancies between the individual analyses. The content of the three main components varied unexpectedly by factors of two to three for the major constituents SiO_2, CaO and K_2O. The repeated results on the standard fly ash (last two columns) clearly show that analytical procedures were not the cause of these highly significant deviations, despite the two different analytical techniques used. Although the fly ash standard does not compare closely in composition to the wood ash, one would be hard pressed

to attribute the highly diverse analytical results to analytical problems only. In this context it is particularly revealing that when the two different laboratories analyse the same ash, relatively consistent results were obtained.

These results forced us to reconsider the entire sampling–handling–subsampling–analysis pathway as implemented in the biomass energy community.

Implications

The study in the original 2009 paper in *Biomass & Bioenergy*[1] was motivated by a failed attempt to mass balance a set of high temperature, partial melting wood ash experiments.[3] The results led to the unexpected indication that appreciable amounts of silica were apparently lost during heating to temperatures of well above 1500°C. Because silica is known to be immobile at atmospheric pressure to very high temperatures, and indeed perhaps *only* volatile at conditions believed to have prevailed during formation of the primitive solar nebula, a second look at the data was warranted. This reconsideration clearly showed that the erratic results were caused by chemical analytical results that were not representative of the biomass investigated. We were able to rule out, using different analytical methods, the possibility that large analytical biases and errors were responsible (Table 1). The conclusion was inescapable: unwittingly large sampling errors were committed by basing our initial analysis on the results from a non-representative primary sampling process.

Because of the heterogeneous nature of the biomass, a grab sample, as is routinely used in this realm, is highly unlikely to be representative for the bulk fuel composition. When we later re-analysed the actual ash used in the experiments and used this composition in new mass balance calculations, we obtained reasonable results that indeed suggested that only the alkali metals were mobile at high temperatures simulating combustion as indeed reported by Thy et al.[3]

This experience prompted us to take a new look into available standard procedures and common practices in related and/or similar studies published in the scientific fuel and biomass literature. A brief survey of papers published in *Biomass & Bioenergy* between 1991 and 2009 showed that very few combustion studies have indeed made the effort to document, far less to ensure,

Figure 1. Air dried wood chips used in the original study. Largest shards are approximately 1 inch (3 cm) in length. Although seemingly of uniform composition, the fuel actually consists of a mix of white fir and ponderosa pine. Grab-sampling of the pristine material will obviously give rise to severe sampling errors (FSE + GSE) if not guided by proper TOS-compliant principles, possibly aggravated by using significantly too small sample masses.

that the biomass material being studied was representative with respect to a particular geographic region or specific location, plant species or the actual power plant fuel intake. Fuel material used in scientific studies is often obtained in limited quantity (~100 kg or less) from forest and agricultural harvest locations or from feedstock intake stations of commercial power plants. Such feedstock samples for forest materials are very unlikely to be representative and to be sufficiently well documented in all relevant aspects. Forest wood fuel is highly heterogeneous (segregated, stratified and contaminated) (Figures 2 and 3) typically composed of components such as pure wood chips, branch and root fragments, bark, foliage, as well as adhering soil. It is neither a simple practical nor an easy intellectual task, if not impossible, to

Table 1. Duplicated analyses of ash fraction of wood fuel (normalised to 100%).

	AN 2002	AN 2005	AN 2006	AU 2002	NIST 1633a	Recom.
Sample size	100 g	100 g	25 kg	25 kg		
SiO_2	33.95	19.89	12.98	14.01	48.61	48.78
TiO_2	0.13	0.33	0.12	0.19	1.37	1.33
Al_2O_3	6.21	9.38	4.11	4.68	27.04	27.02
Fe_2O_3	2.43	3.60	1.40	1.71	13.63	13.44
MnO	2.01	1.99	2.66	2.64	0.02	0.02
MgO	4.33	10.05	7.02	7.39	0.79	0.75
CaO	35.67	23.92	47.40	48.04	1.56	1.55
Na_2O	0.58	0.60	0.63	0.58	0.21	0.23
K_2O	11.36	20.08	18.42	16.06	2.23	2.26
P_2O_5	3.33	10.18	5.25	4.69	0.38	0.38
Sum	100.00	100.00	100.00	100.00	95.84	95.76

Recommended composition of NIST 1633a (coal fly ash) are from GeoReM (2006) (http://georem.mpch-mainz.gwdg.de). Other analyses are from Thy et al.1

aim for the proverbial statistically sound "random and representative" sample from such materials. This would require that the probability of all individual "elements" being sampled is exactly identical, irrespective of size, shape and their constituting elements (wood chips, bark, leaves, roots). In fact, the heterogeneity of biomass feedstock easily ranks among some of the most difficult materials to sample (Figures 2 and 3). In such a context, the unwitting quest for an intuitive and simple sampling procedure will always be on the agenda. This may have been a major scientific hindrance wherever reliable analytical results were essential for achieving a specific goal.

Without knowledge and respect for proper sampling principles, selection of supposedly representative samples all too often boils down to a personal intuitive judgement tied to the purpose of the particular study at hand, and this is almost invariably carried out by grab-sampling. If it is intended that the primary sample will represent the specific part of a forest, or a specific tree species, it may perhaps be possible to design a spatially random sampling strategy based on statistical knowledge from forest biomass surveys. Most likely it is more often desired that a sample should represent a specific biomass type and/or a seasonal average intake at a power plant (such as spring white pine wood). It is often possible to get sampling access to the feedstock at either an intake station at a

power plant or from a conveyor belt prior to being admitted to the boiler. But to conduct representative sampling at such locations is still considered a daunting task for which most investigators often do not have the knowledge, patience or means to succeed. Because few fuel laboratories possess the required facilities for storing, preparing, ashing and sampling large fuel volumes for study and analysis, there is little doubt that truly representative samples are considered merely an ideal and unobtainable dream for many combustion studies of biomass fuels, whether originating from agricultural or urban sources.

Many investigators likely proceeded as was done in the original study: with the kind help of a plant fuel intake manager, we obtained a few, large plastic containers with wood chip feedstock claimed to be "as received" at the plant from a typical supplier. The information obtained in our case was that it represented mixed conifers (white fir and ponderosa pine) harvested from the north-eastern slopes of Mount Shasta, California. There is an almost unavoidable tendency to trust such claims regarding the provenance of primary samples, if not experienced regarding proper sampling principles, but this is most often a fatal trust. The fuel in our case was a high quality, whole-tree fuel composed of relatively clean wood chips with limited bark, branch and foliage parts. We proceeded to process about 100 kg of this fuel, which was the maximum

that could reasonably be handled with the available facilities. We ashed a rather large proportion (25% of the primary sample mass) and were reasonably confident that the resultant ash after homogenisation and the sub-samples subsequently taken, represented the fuel, i.e. the secondary and tertiary sampling/mass-reduction steps were reasonably in control. There is no knowledge, however, of the degree to which the fuel truly represented the harvest biomass, the fuel received at the plant, the fuel conveyed to the boiler or combinations thereof. The primary sampling accuracy and hence the *representativity* may thus literally have been lost in the woods.

Discussion

The critical question obviously is whether the biomass field can live with this kind of uncertainty. Most of the scientific endeavours are designed toward understanding combustion and gasification processes and not toward obtaining absolute and truthful values representing the original feedstock fuel. The interest is most often to understand how certain elements behave during thermal conversion. The answers that we are seeking are thus typically relative to specific processes and not absolute with respect to original lot materials. Often secondary sampling from a primary sample (which may be more-or-less representative with respect to the primary lot) appears to provide an acceptable basis for this kind of specific studies, allowing us

Figure 2. Typical fresh wood chips characterised by significant proportion of bark and foliage. Grab-sampling of this type of material will give rise to severe sampling errors (FSE + GSE) if not guided by proper TOS-compliant principles. Add hereto Incorrect Sampling Errors (ISE) if not considered.

Figure 3. Typical wood shard bio-fuel at a power plant intake. At this plant, routine primary sampling (for moisture determination), takes place following fully TOS-compliant procedures, see Reference 4 for details. An incremental primary increment sampler is shown (centre) just before being inserted into the lot (truckload); the sampler is closed when inserted. Three increments are used for composite sampling, i.e. from the top, middle and bottom level, respectively, with random sampling location in the X–Y plane.

to gain insight into the central processes as long as fuel and products are sampled and handled in a sensible and identical representative manner from the secondary sampling stage onwards.

The seasoned experimentalists may advise that instead of trying to understand the behaviour of heterogeneous fuel systems, one may gain a better understanding of compositional variables by studying the individual components before embarking on the daunting task of examining experimentally the full complexity of realistic multi-component fuel systems. This way one can build an understanding of the complex system from knowledge of the behaviour of the individual components (bottom-up approach). Such an approach will also reduce the problem of obtaining representative components as long as we can sort and purify the material into its separate constituents. This bottom-up principle has been highly successful in phase equilibria studies of silicate systems, either simple or complex, and many other types of material science studies. However, at the end of this endeavour we are still left with the challenge of accounting for the total system in industrial use. In the understanding of biomass combustion, as well as in most other areas of science, the summation of all parts is often likely to be considerably more complex than a mere aggregation of partial results.

Thus, irrespective of method, scope and goal, it is critical for future biomass studies relying on analyses of experimental products that these be sampled only in a representative manner. This involves representativity in sampling of the primary lot, as well as for subsequent splitting of potentially large volumes (secondary sampling), milling of sub-samples to workable particle sizes and homogenising before the ultimate analytical aliquots are taken. In some cases it may be advantageous that sampling is done on ash fractions despite potential loss of elements during ashing, because smaller volumes and finer grain-sizes are easier to handle and ashes results in lower analytical detection limits. But relatively small grab samples of raw biomass or ash are, as shown also by our own experiences, prone, indeed likely, to be *non-representative* and may thus exhibit strongly diverse compositional variations. This is particularly true for the elemental composition of an ash fraction that only constitutes a minute proportion of the total sample (the ash fraction of clear wood is typically below 0.2). An increase in primary

sample volume is often the only variable known that is believed to bring down these compositional sample-to-sample variations, but in fact this will only be true for samples approaching the total volume. A scientifically founded and improved sampling must counteract every feature of the complex lot heterogeneity, e.g. as per the principles presented in DS 3077.[2]

It is an essential, key insight in particular for all significantly heterogeneous materials, which cannot be freely mixed before the primary sampling stage (either too large and/or too heterogeneous lots), that composite sampling is the *only way forward*. A particularly relevant example is provided by Møller and Esbensen[4] for the primary characterisation of intake wood chips at a Danish power plant (Figure 3).

Conclusions and recommendations

Studies of biomass combustion processes are critically dependent on whether analyses of primary fuel (and ashes and slag) are conducted on samples that are demonstrably representative for the processes and materials being studied. The inherent problems in conducting traditional "statistically and sound sampling" of highly heterogeneous and stratified biomass critically restrict our ability to design valid and meaningful experiments of combustion processes. It is sometimes suggested, as a first alternative, that studies are conducted on the individual fuel components before multi-component fuel systems are being investigated, but

this approach only dodges the ultimate purpose and will not necessarily address the full problem at power plant or incinerator plant scales. Consideration of proper mass reduction procedures (secondary sampling and sampling preparation) is still a prerequisite for the success of all biomass related studies. For this demand, as well as for primary sampling issues, a consistent theory of sampling is critically needed. There is an overwhelming TOS literature available to everybody's needs, a judiciously selected part of which can be found referred to in DS 3077.[2]

References

1. P. Thy, K.H. Esbensen and B.M. Jenkins, "On representative sampling and reliable chemical characterization in thermal biomass conversion studies", *Biomass Bioenerg.* **33**, 1513–1519 (2009). doi: 10.1016/j.biombioe.2009.07.015

2. *Representative sampling—horizontal standard*. Danish Standards DS 3077 (2013). Technical abstract: http://webshop.ds.dk/product/M278012/ds-30772013.aspx

3. P. Thy, B.M. Jenkins, C.E. Lesher and S. Grundvig, "Compositional constraints on slag formation and potassium volatilization from rice straw blended wood fuel", *Fuel Process. Technol.* **87**, 383–408 (2006). doi: 10.1016/j.fuproc.2005.08.015

4. H.S. Møller and K.H. Esbensen, "Representative sampling of wood chips", in *Proceedings 2nd World Conference on Sampling and Blending (WCSB2)*, AusIMM, pp. 255-208 (2005). ISBN 1920806288. A reprint is available from the authors.
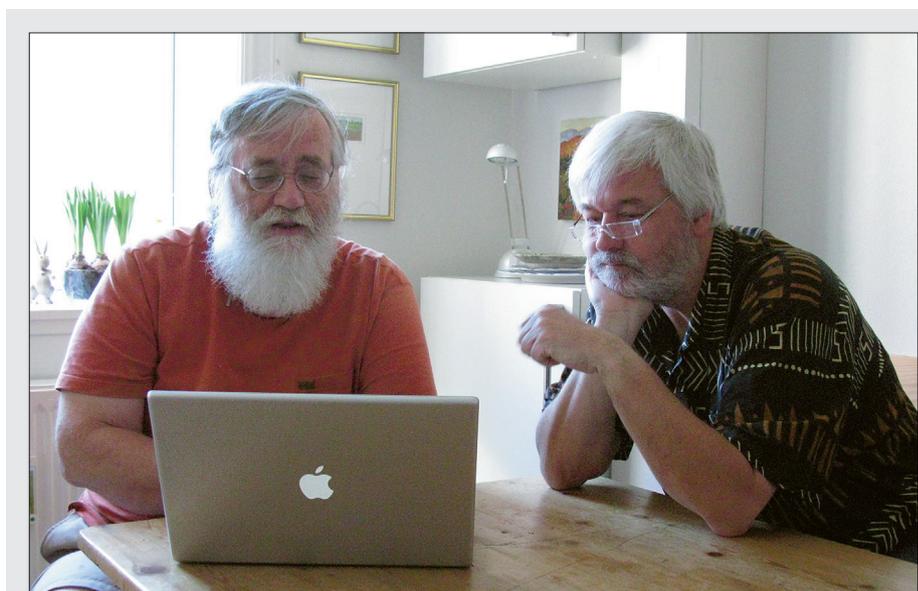
The authors (Peter Thy, left): "WHOA—factors 2–3× wrong due to inappropriate sampling".