

**Project no. 038644**  
**Bio-Norm II**

**Pre-normative research on solid bio-fuels for improved European standards**  
**SPECIFIC TARGETED RESEARCH OR INNOVATION PROJECT**  
**PRIORITY [6-1] – Sustainable energy systems**



**General guidelines on developing and applying sampling to investigate inter-lot variances for solid biofuels**

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Revision 1

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## Involved Participants

The following institutions have been involved in the generation of this deliverable:

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## Revisions

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|         |            |                  |        |

## 1 Background

The overall aim of the BioNorm II project was to carry out pre-normative research in the field of solid biofuels in close collaboration with the work of CEN TC 335 "Solid Biofuels". Due to the wide range of standards to be developed by CEN TC 335 this project was focused on such aspects urgently needed by industry to increase the markets for solid biofuels where significant pre-normative R&D need was given.

To achieve these goals, the following aspects needed to be addressed in detail:

- further improvement of existing reference tests in particular in terms of precision,
- development of new reference test methods,
- development of rapid on-site test methods,
- development of sampling and sample reduction methods for further materials and development of sampling plans,
- development of quality measures in accordance with the ISO 9000 family especially adapted to solid biofuels.

To develop this information, the following Work Packages have been carried out:

1. WP I "Sampling, sample reduction and sample planning"
2. WP II "Test procedures"
3. WP III "Quality measures"
4. WP IV "Biofuel specifications"

## 2 Results obtained in WP I Sampling, sample reduction and sample planning

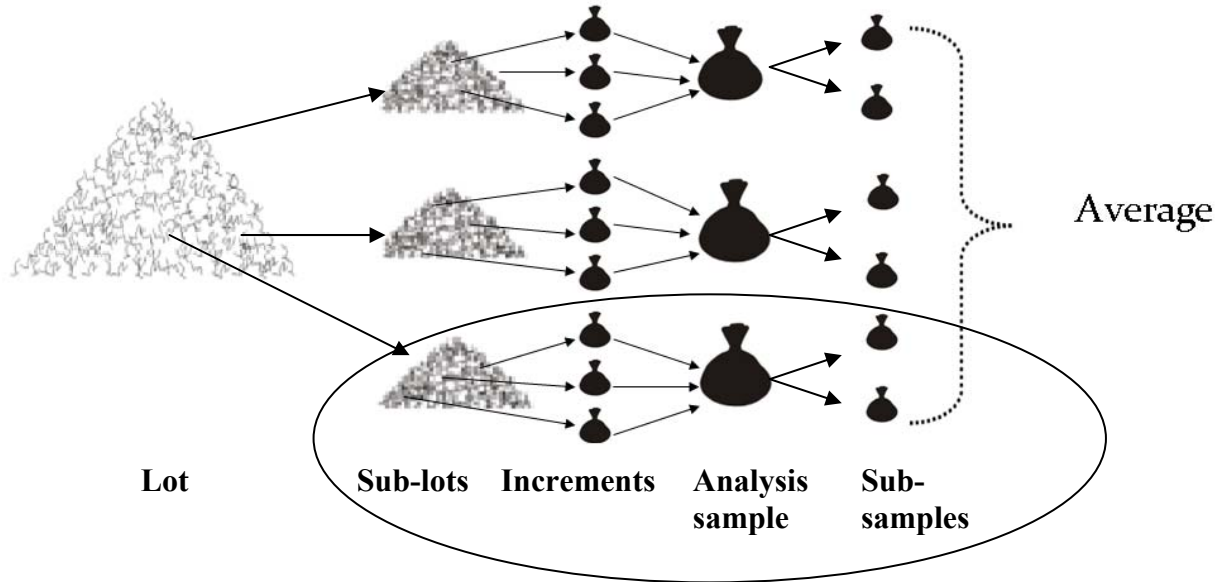
### 2.1 Sampling

It is well known that the sampling step constitute a great source of error in the characterisation chain of a solid biofuel. This measuring error may be divided into two types, namely systematic error or bias, and experimental error. Bias affects the accuracy (how close the average of the analytical result is to the “true value”), and is often caused by a single factor like erroneous calibration, inappropriate analytical method, incomplete dissolution of the sample, misrepresentative sample, etc. This error gives rise to an analytical result that is always too low or too large compared to the “true result” and should always be eliminated as far as possible.

Experimental error on the other hand is due to several factors where each factor has small impact on the result and may affect the result in both positive and negative direction. Examples of such factors are variations in humidity, ambient temperature, etc. This type of error does not influence the accuracy of the analytical result as the bias does. Instead the experimental error affects the precision, which is the distribution of the analytical results around the “true value”. A low precision means that the results from repeated analyses have a large spread around the “true value” and vice versa. Experimental errors cannot be eliminated, but can be handled by suitable statistical methods.

The sampling of a solid biofuel is usually carried out as described in figure 1. From the original lot, a number of sub-lots are taken. From each sub-lot a number of increments are

sampled and aggregated to an analysis sample. This analysis sample is then divided into a number of sub-samples which are used for the analyses of the parameters of interest, i.e. moisture or ash content.



**Figure 1** Description of common sampling schemes for solid biofuel.

The uncertainty of a specified analytical parameter in the lot can be calculated from

$$e = 2 \cdot \sqrt{(\sigma_N^2/N + \sigma_I^2/NI + \sigma_T^2/NT)} \quad (1)$$

Where

$e$  = precision (twice the standard deviation) for the specified analytical parameter

$\sigma_N^2$  = sub-lot variance for the specified parameter

$\sigma_I^2$  = increment variance for the specified parameter

$\sigma_T^2$  = sub-sample test variance for the specified parameter

$N$  = number of sub-lots averaged

$I$  = number of increments per sub-lot

$T$  = number of sub-samples per increment

A special case of the above sampling scheme is when you only are interested in the result for the sub-lot (encircled in figure 1). In that case the formula for the uncertainty is

$$e = 2 \cdot \sqrt{(\sigma_I^2/I + \sigma_T^2/T)} \quad (2)$$

Where the included parameters are defined as above.

To be able to obtain a required precision of a specified parameter it is necessary to have information of the individual variances  $\sigma_N^2$ ,  $\sigma_I^2$ , and  $\sigma_T^2$  of that parameter. A suitable experimental design to acquire this information is a nested (hierarchical) design described in

Box et al (1) which is evaluated by using the statistical method Analysis of Variance (ANOVA).

In the design used in WP I Task I.1 five sub-lots of six different materials were studied by sampling four increments from each sub-lot using two different sampling methods; heap sampling and conveyor sampling. The six materials were bark from pine, wood chips from conifer, 8mm pellets from conifer, 6mm pellets from beech, olive residue and grape residue. Each increment was then divided into two sub-samples and the sub-samples were analysed once for 3-10 analytical parameters depending on the material. A detailed description of the experimental design may be found in the delivery D.I. 8 Statistical analysis.

The results from the sampling experiments may be summarized as follows:

No significant relative bias between the sampling methods was obtained except for the analyses of particle size distribution in wood chips and the mechanical durability of 8mm pellets. The reason to this discrepancy is the segregation of small and large particles in the heap.

In general, no significant difference in precision between the sampling methods was found except for some of the elements in grape and olive residue. However, in many cases these differences were contradictory and no clear trend was obtained.

The comparison of the precision between the increment sizes did not show any clear trend even if the smallest increment size, in general, had the greatest variation.

In table 1 the individual variances for sub-lots, increments and sub-sample tests are calculated from the results in Task I.1 for moisture and ash content in the six materials. Corresponding variance values were calculated for the other analytical parameters.

**Table 1** Individual variances for sub-lots, increments and sub-sample tests for moisture and ash content in bark, wood chips, 8mm pellets, 6mm pellets, olive residue and grape residue.

| Biofuel              | Moisture (%) |              |              | Ash (%)      |              |              |
|----------------------|--------------|--------------|--------------|--------------|--------------|--------------|
|                      | $\sigma^2_N$ | $\sigma^2_I$ | $\sigma^2_T$ | $\sigma^2_N$ | $\sigma^2_I$ | $\sigma^2_T$ |
| <b>Bark</b>          | 3,12         | 4,89         | 0,68         | 0,383        | 0,026        | 0,019        |
| <b>Wood chips</b>    | 1,98         | 10,5         | 0,058        | 0,027        | 0,023        | 0,0004       |
| <b>Pellets (8mm)</b> | 0,800        | 0,158        | 0,003        | 0,0050       | 0,0004       | 0,0003       |
| <b>Pellets (6mm)</b> | 0,008        | 0,016        | 0,014        | 0,0004       | 0,0004       | 0,0071       |
| <b>Olive residue</b> | 0,120        | 0,105        | 0,028        | 0,832        | 0,658        | 0,527        |
| <b>Grape residue</b> | 6,06         | 0,746        | 1,88         | 0,198        | 0,519        | 0,202        |

The minimum number of increments to be taken from a lot or a sub-lot of a biofuel material to obtain a specified precision of the analytical parameter of interest depends on the heterogeneity of that parameter in the material in combination with the design of the sampling method.

This minimum number of increments is determined by the sub-lot variance ( $\sigma_N^2$ ), the increment variance ( $\sigma_I^2$ ) and the sub-sample variance ( $\sigma_T^2$ ) of that parameter, respectively, together with the number of sub-lots averaged ( $N$ ) and the number of sub-samples analysed ( $T$ ) according to the following formula.

$$I = \frac{4\sigma_I^2}{Ne^2 - 4\sigma_N^2 - \frac{4\sigma_T^2}{T}} \quad (3)$$

For the special case shown in figure 1 the corresponding equation (4) is

$$I = \frac{4\sigma_I^2}{e^2 - \frac{4\sigma_T^2}{T}} \quad (4)$$

The definitions of the included parameters are the same as above.

## 2.2 Sample reduction

During the sample reduction of the analysis sample to sub-samples it is important to use a method that retain the representativity of the original sample and result in a high precision between the reduced samples.

In WP I Task I.1 the precision of three different sample reduction methods were examined on the six materials mentioned in 2.1. A homogenized analysis sample was divided into 16 sub-samples by using the sample reduction methods coning & quartering, long pile and riffle box, respectively. Each sub-sample was analysed for 2-4 analytical parameters and the standard deviation of the analytical result was calculated.

The results showed that no reduction method was significantly better than the other two when comparing the precision of the analytical results within a material.

## 2.3 Sample planning

The sampling experiments described in section 2.1 were carried only during one week. To verify these results long time experiments (Task I.2) were performed where 1-4 samples per week during 5-12 weeks were collected depending on the material. The samples were analysed for the same analytical parameter as in section 2.1 and the overall standard deviations and the sub-sample test standard deviations were calculated and compared to the results in Task I.1.

No significant difference between the standard deviations in the two tasks was found except for olive residue and 6mm pellets. The reason to the discrepancy was that the olive residue was sampled from two different shipments with different origin and that the 6mm pellets was sampled at two different pellet plants that were using two different types of raw material.

### 3 General guidelines on developing and applying sampling to investigate inter-lot variances for solid biofuels

Referring to the above summary of the results, and the deliveries D.I. 8, D.I. 10 and D.I.12 the following general guidelines on developing and applying sampling to investigate inter-lot variances for solid biofuels are suggested:

- Since the results from BioNorm II WP I should be treated as representative only for the biofuel material studied in this project, it is recommended that a corresponding investigation is performed to evaluate the individual variances  $\sigma^2_N$ ,  $\sigma^2_I$  and  $\sigma^2_T$  for the calculation of minimum number of increments of any new material of interest. This is valid also for materials studied in this project, where it may be suspected that the properties differ considerable.
- If a separate investigation is outruled, the variance values evaluated in WP I can be used to get an idea what sampling parameters have to be used to obtain a required level of precision for a certain biofuel material.
- If possible it is recommended that the sampling is performed from a moving stream, i.e. a falling stream, where each particle of the material has an equal probability of being included in the sample. This is important especially for analytical parameters where the sizes of the material are involved in the analysis, i.e. particle size distribution and mechanical durability of pellets, since small and large particles have the feature to segregate when they fall into a heap. However, if the sampling from a moving stream is not possible, this project has shown no significant bias between the sampling methods, heap sampling and conveyor sampling, for most materials and parameters.
- The choice of minimum increment size should be calculated from the formulas in the technical specification CEN/TS 14776-1:2005 (2)

$$V_{\min} = 0,5 \quad \text{for } d < 10$$

$$V_{\min} = 0,05 \times d \quad \text{for } d \geq 10$$

Where

$V_{\min}$  is the minimum increment size, litre

$d$  is the nominal top size, mm

However, if the material shows considerable heterogeneity the increment size should be increased to improve the precision of the analyses. It may also be noted that the increment size together with the increment number shall be chosen so that the required sample size for the analyses of interest is obtained.

- The sampling site should be chosen so the best answer to the specific issue is obtained.