

# Characterization of Solid Biofuels 2004 – Development of Methods

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Summary Report and Guidelines

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Appendix 1: Detailed instructions for sampling of solid biomass fuels  
(Compendia of 4 papers on the Theory of Sampling)

Appendix 2: Guideline for the determination of internal particle size of fuel pellets

Appendix 3: Guideline - Solid biofuels – Determination of visual recognisable impurities > 2 mm

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## 1. Abstract

To facilitate trade in solid biofuels across regions and borders with different national practices, it is increasingly necessary to instate common standards for measuring the tradable qualities.

In this solid biofuel characterization project we identified core parameters for comparison of solid biofuel quality, e.g. internal particle size distribution in pellets, slagging tendency, heat value and water content. The main focus has been on developing methods for sampling and measuring in a consistent way that can be uniformly adopted by new traders and buyers entering this field.

The very many differences between coal and solid biofuels came as a surprise to the power industry when we first started co-firing straw in coal-fired boilers. After all, they are made of the same original organic materials. But it was soon clear that particle size, important for surface ignition and movement pattern in the furnace, was very hard to describe with the methods know from coal firing.

It was also apparent that the simple business of taking a representative sample from a coal delivery was not transferred easily to bales of straw or loads of pellets. Water content throws the sample uniformity off extremely easily. Foreign objects got caught in the baling process. The lower half of a stack could be dry but the top dripping wet.

The challenge has been to mainstream the characterization procedures into comparative parameters to simplify the trading and level the expectations between sellers and buyers in a way that allows the plant operator to plan out the fuel mix and get the predicted results.

European standardization of solid biofuel started more than ten years ago. However, in order to make the standards, necessary research had to be performed. Research projects like Bionorm I and Bionorm II have been made at European level. The results presented in this project are from a Danish solid biofuel characterization project. Several parameters identified in this project need further investigations by the Danish partners.

Due to the very extensive material produced in this project (> 1000 pages) this report is a summarizing report derived from 5 extensive reports of each major work packages (1, 2, 3, 4.1 and 4.2). This report does thus focus on summarizing the general aims, major results and conclusions from the project but giving enough details and information so it can be read as a stand-alone report. An important task of the project was to develop guidelines for improved and correct methodologies to characterize solid biomass fuels. These guidelines which derive from the tests and results from the project are therefore included as appendix to this summarizing report.

### 1.1 The main aims of the project

PSO project 5297 is dedicated to the development of new methods and techniques used to sample and characterize biomass for relevant qualities. It was the aim to elaborate on this topic by the performance of a number of activities divided into 4 main work packages (WP).

The overall aim of **WP1** was to test if the quality of currently used sampling methods of solid biomass fuels is sufficiently enough. Which quality demands can be put on a correct sampling?

Based on these results the aim was to suggest correct methodologies and protocols for future sampling of different solid biomass fuels and delivery sizes.

The general aim of **WP2** was to determine the size distribution of particles smaller than 3.15 mm which is especially important for pulverised fuel combustion. Furthermore, the aim was to determine the internal size distribution of particles in solid biofuel pellets as well as the amount of external contaminants in solid biomass fuel samples (e.g. sand and gravels).

The wide-ranging aim of **WP3** was to investigate different methodologies to determine ash melting of different kinds of biomass fuels as well as development of new fast methodologies suitable for quick analysis at fuel reception revealing any contaminations of the fuel (e.g. dirt from incorrect handling or use of illegal raw material).

The aim of **WP4.1** was to investigate methods to determine biological origin and biodegradability of biomass waste fractions in order to be able to account for their CO<sub>2</sub> neutrality. This is driven by the aim of being able to follow the new rules of the Kyoto protocol for CO<sub>2</sub> quotas for waste combustion plants exceeding 20 MW.

The aim of **WP4.2** was to investigate and document the potential of utilizing online Near Infrared Spectrometry (NIR) for determination of the primary quality parameters: Water, ash and calorific value of wood pellets and secondary main elements and chosen trace elements.

Each of these work packages are subdivided into further underlying specific aims and tasks which are described more detailed in the subsequent sections of this report.

## **1.2 Short summary of work content and results**

The work of **WP1** comprised detailed elaboration on representative sampling of solid biofuels such as wood pellets and wood chips at existing facilities in Denmark. After introductory studies of existing literature (standards and guidelines) for sampling biomass, the present project based its work on the Theory of Sampling (TOS) instead of continuing to elaborate on the previous standards. New specifications and methodologies were therefore developed and tested, evaluated and verified by sampling of wood pellets at Fredericia and Kolding harbour, at the Avedøre power plant as well as sampling of wood chips at the Herning power plant. Sampling errors and heterogeneity were evaluated in 1-D (sampling of biomass in motion, e.g. conveyor belt) for wood pellets and in 3-D (sampling of biomass from stationary piles, stacks, lots, etc...) for wood chips in containers.

The methodologies used are summarized in a compendium describing the principles behind the Theory of Sampling and summarised as practical guidelines for sampling of biomass. Results from the investigations were evaluated using variography. A variogram contains all information required to estimate the total sampling error (TSE) for the commodity in question (here wood pellets is used as the prime example), and the uncertainty of the analysis result was calculated for alternative sampling schemes. This made it possible to choose a sampling scheme that precisely matches the requested accuracy and precision.

In order to determine how biomass sampling takes place today in Denmark, selected players within trade, production and use of solid biofuels have been interviewed; three importers, three producers and four end-consumers.

The project's evaluation of existing methods, supported by the industry sector interviews, firmly points out that a paradigm shift is needed: Instead of continuing to develop *local* (i.e. matrix-dependent) sampling standards, what is needed is a *universal* so-called "horizontal standard". The results in WP1 constitute the first of such attempt.

In the work of **WP2** different methods for particle size distribution, such as mechanical sieving, sieving in an air stream and by means of image analysis (Camsizer) were developed, tested and evaluated. The investigations comprised biomass samples of wood dust and comminuted straw. The results were statistically evaluated and revealed a larger deviation in the particle size distribution for straw than for wood. Some methods such as sieving by air jet was not suitable for straw at all.

Moreover, WP2 also includes work on finding the best methods for disintegrating pellets and analyzing the size distribution of these particles. Screening investigations were carried out of different methods for disintegrating wood pellets by dissolving the pellets in water and subsequently analyzing the particle size distribution. The best method was tested and developed further in Round Robins in collaboration with European laboratories. The results were summarized and form the basis for suggestion of a new CEN Technical Specification. Comparison between particle size of wood particles in wood dust prior to pelletizing and the particle size of disintegrated pellets was also conducted. The results revealed a smaller particle size distribution of the saw dust particles after pelletization as well as after milling of the pellets at the power plant compared to the saw dust used for the production of the pellets.

The third part of WP2 was focusing on investigating methods for determination of coarse (> 2 mm) and fine impurities (< 2 mm) in biomass fuels. The investigated methods comprised determination by visual inspection, wet sedimentation, chemical determination, and utilization of seed cleaner machinery as well as a stepwise methodology using combinations of mechanical sieving and air separation. For determination of coarse impurities a method was elaborated based on mechanical sieving, including attempts of re-finding added impurities showing that it is possible to identify and quantify impurities with a nominal top size > 2 mm using the developed method. Subsequently, final instructions for the tested method have been elaborated in "Guideline – Solid biofuels – Determination of Visual Recognizable Impurities > 2 mm".

Wet sedimentation, chemical separation and separation in vertical air flow were tested but were all concluded not suitable for the determination of fine particular impurities in solid biofuels. Due to this a prototype has been designed based on a separation in horizontal air flow instead. Since the prototype was not quite finished by the end of the present project, no testing has been carried out. As the method principle is found to be promising for a determination of the content of fine impurities in solid biofuels, further work within this matter will continue under management of the European project BioNorm II.

The work of **WP3** was focused on finding methods for characterizing the melting of ash in biomass and the influence of contaminants and additives such as soil, dirt, gravel and kaolin. For this purpose 7 typical wood and herbaceous (straw and kernels) biomass fuels were collected and

analysed with the different methodologies of WP3, both as pure as well as mixed with contaminants and additives. Different methods for determining ash melting and potential slagging of biomass were investigated and compared to the standard CEN/TS 15370-1. The investigated methods comprised analyses in specially developed apparatus such as the Melt Area Fraction analyser (MAF) and the Slagging Analyser. In addition to these methods, “simple” methodologies using standard laboratory equipment were developed and tested. These methods comprised a “Simple Slagging Test” based on combustion of small samples in ceramic crucibles, a “Simple Salt Test” based on conductivity of dissolved ash in water solutions and a “Simple Salt Ion Test” which is based on standard qualitative chemical analyses.

The results from the different types of analyses are complicated to compare as they are all relative laboratory methods and thus only trends and comparative tendencies can be compared. The overall results from the methodologies tested reveal that more molten ash at lower temperatures is detected for the herbaceous biomass than for the woody fuel. The addition of contaminations and additives had different effects depending on which biomass they were added to. While addition of contaminants such as gravels and soil lowered the initial melting temperature for woody biomass, it increased it for the herbaceous fuels. The effect can be explained by that molten ash origin from woody biomass is dominated by silicate-based melts and the initial molten ash from pure herbaceous is based on alkali salts. By addition of contaminants such as soil and gravels, which contain high amounts of silica-containing minerals, the system is moved from the salt-dominated system with possible melting eutectics temperatures, typically around 700 - 800 °C towards the silicate-based systems which have melting temperatures typically starting at about 900 – 1000 °C and above.

In addition to the above-described methods for determining ash melting temperatures two types of XRF techniques, wave length dispersive (WD) and energy dispersive (ED), were investigated as potential fast methods for onsite detection of quality and contamination of biomass. Detection limits, accuracy and comparison to conventional wet chemical analyses were tested and evaluated for both systems. The results revealed limitations for detection of lighter elements, especially Si, but they also showed great potential for using these methods for onsite screening analyses of biomass.

The work of **WP4.1** investigated the present status of methods for analysis of the biomass content of waste derived fuel for being able to determine the percentage of CO<sub>2</sub> neutral emissions during combustion.

During the project, technical specifications have been published for analysing and calculating the biomass part of waste derived fuel.

One of the methods is described in the specification CEN/TS 15440 and is based on chemical degradation of the biomass content using a rather simple laboratory method, which can be used in the company laboratories. However, the error in the estimated biomass content is significant for a number of waste materials. An example is polyurethane waste which by the method is characterized as nearly 100% degradable and thus classifies the waste to biomass although it is based on fossil fuels. Test of the method shows larger errors when working with mixed waste than indicated in the specification for the individual waste types. Suggestions for improvements of the method are described.

The biomass part can also be analysed using a <sup>14</sup>C (carbon-14) based reference method. Advantages and disadvantages of the two methods are being discussed. As an example, the error in estimating

the biomass part by the chemical degradation method is assessed for household waste added to Danish incineration plants based on collected data for the waste composition in Denmark.

Finally, the possibility of developing methods based on enzymatic degradation is studied.

In **WP4.2**, test and development of non-contact, on-line analyzing of biomass properties with Near Infrared Spectrometry (NIR) was conducted. Initially, the instruments were established in the laboratories of the Danish Technological Institute where a preliminary investigation was performed. After successful detection and modelling of water content, ash content and heating value, the equipment was subsequently installed above a belt conveyor after a silo at Køge Biopellet factory. Reference samples were taken regularly for analysis of water content, calorific value and ashes for the control and further development of the NIR calibrations. The calibrations were currently developed and the functionality of the NIR instruments evaluated. The introductory investigations of the on-line NIR equipment at the Danish Technological Institute indicated that it is possible to develop calibrations for both instruments as regards water, calorific value and ashes.

The investigations at Køge Biopillefabrik showed that it is possible to establish a non-contact on-line NIR measurement of water and calorific value of wooden pellets above a belt conveyor. Both NIR instruments can manage the task tending towards better or more robust calibrations of the MATRIX-F instrument.

### 1.3 Main conclusions and suggestion for future work

The major conclusion of the work of **WP1** is that **representative** sampling of biomass fuels and its potential effect on the analysis results are not guaranteed by the current standards for sampling and analysis of biofuels in bulk. Moreover, during the work of WP1, conclusion early arrived at a paradigm shift: It is no longer tenable to rely on matrix-dependent standards for sampling solid biofuels. The only scientific and practical guarantee for representativeness is the Theory of Sampling, TOS, which must therefore be inducted as the universal framework for sampling.

This empirical work of WP1 clearly illustrates this. These findings and conclusions are summarized in a number of published articles which together comprise specifications for measures necessary to secure representative sampling of wood pellets and wood chips (Appendix 1).

These specifications are based on the principles in TOS, and a set of descriptions providing specific instructions in what measures to take in order to develop a sampling scheme that lives up to a specific sampling situation. These specifications also includes instructions on how to evaluate the sampling using variogram techniques which is a fundamental tool to describe aspects as autocorrelation between increments, calculation of minimum achievable sampling error and calculation of the overall sampling error of any sampling scheme, which is relevant for the commodity in question.

As examples of how TOS can be used in practice to develop a sampling scheme, the project reviewed 1-D sampling of wood pellets during transportation and 3-D sampling of wood chips from a stationary container.

In principle it is much more difficult to ensure a representative sample from stationary materials but there are technical solutions that have proven to work satisfactorily in practice. Compared with 1-D sampling it takes far more resources to carry out 3-D heterogeneity characterization; however, knowledge of the heterogeneity aspects of the biomass are critical since the inherent heterogeneity of the biomass gives rise to the errors that arise in all sampling procedures.

A detailed 3-D heterogeneity characterization focusing on the moisture content of wood chips was performed which clearly demonstrated a highly heterogeneous distribution in a container (truck load) of wood chips. This study emphasised the importance of being able to derive representative sampling procedures when meeting a new material, a new lot, or any other material which has not been properly sampled before and underlined the degree to which much of the existing literature about biomass sampling is insufficient and sometimes directly misleading.

1-D sampling of wood pellets was conducted at reloading at harbours. Compared to 3-D sampling this is much simpler to ensure representative sampling (**i.e. equal chance for all particles of the biomass to be extracted**). By this approach it is also possible to carry out heterogeneity characterization using the variogram technique.

The harbour investigations revealed that current manual sampling with spear or bucket sampling of pellets is not satisfactory for representative sampling. It is **strongly recommended** that new mechanical sampling from moving flows of pellets is to be implemented **in the future**.

This need for improved sampling procedures and methods including practical guidelines was confirmed by interviews with 10 biomass market actors.

In **WP 2.1**, wood dust and comminuted straw. The size distribution was determined by mechanical sieving in sieving tower by Alpine air jet sieve and by image analysis in a Camsizer.

Mechanical sieving is a simple and cheap method for control of the size distribution of a material, and opposite to the image analysis the fractionation takes place according to the width of the particles. The image analysis offers more detailed information including number and shape of the particles. This is particularly interesting from an application-technical view where number and shape of the particles in the different sizes are important parameters for dust firing. Determination with the Alpine air jet sieve did not result in improved results to support the choice of air jet sieve as a method for determining the particle size distribution.

In **WP 2.2**, a method has been developed for determination of the particle size distribution in fuel pellets through disintegration of the three tested pellet types, respectively hard wood, soft wood and straw pellets. Based on the fact that these specific types of raw material is representative for the primary market for commercially available fuel pellets world wide, it is concluded that the method is suitable as basis for a European standard for determination of the particle size distribution of the raw material of solid biofuel pellets.

In **WP 2.3**, a method has been elaborated for determination of the content of coarse impurities with a nominal top size above 2 mm in biofuels. Furthermore, a proposal has been developed for a principle for a stepwise determination of particular impurities with a nominal top size below 2 mm. For the method principle's step 2 there is designed a prototype of equipment used for determining the fine particular impurities, which will be examined under management of the European project BioNorm II.

As a result of *Work Package 2 Physical Characterizations of Biofuels* the following has been elaborated:

- Essential proposed amendment for the future EN standard for determination of particle size distribution in solid biofuels with a nominal top size less than 3.15 mm, draft CEN/TC 335 N174, 2008-01 Solid Biofuels – Part size distr. 2 (AP2.1).
- Guideline for the Determination of Internal Particle Size of Fuel Pellets (Appendix 2).
- Guideline – Solid biofuels – Determination of Visual Recognizable Impurities > 2 mm (Appendix 3).
- Principle for a stepwise determination of particular impurities in primarily wood chips and other wood-based fuels and design of prototype for determination of fine particular impurities, cf. above.

**Future works** related to WP2 should focus on developing online test methods for characterizing physical parameters for solid biofuels. Promising methods would be NIR and acoustic methods which could describe the moisture, mechanical durability and amount of fines which all are main quality characteristics of solid biofuel pellets. If successfully implemented, such methods could

contribute substantially to improve the quality control at the gate and during combustion and production of solid biofuel pellets in the industry.

In **WP3** three new ash melting test methods, MAF, Slagging Analyzer, Simple Slagging Test and the current standard method CEN/TS 15370-1 were tested on a set of seven different biomass samples with and without additives and contaminations chosen to influence the melting behaviour of the ash. While the long-term aim of these methodologies is to be able to predict slagging and fouling potential from laboratory analyses of biomass samples, the short-term aim (which was investigated in this project) was to test and prove the usability of these methods in terms of detecting relative behaviour of the investigated samples as well as detecting effects of contaminations.

The general results revealed that wheat material (straw and kernels) typically has much lower melting temperatures and higher slagging potentials than woody biomass fuels and rape straw. Addition of contaminants to woody biomass and rape straw fuels decrease their melting temperature while the effect is generally the opposite for the wheat materials.

It was concluded that due to the special features of each of the different methodologies it is difficult to perform direct comparison of all the methods. E.g. while the CEN/TS 15370-1 method is able to reveal points concerning initial melting temperatures of ash mixture (DT, HT and FT), the MAF method is able to detect if more than one melting phase is existing in the ash sample and also give information on the melting behaviour over the whole temperature scale. Thus when more detailed information is required, the MAF is the more suitable method. While both the MAF and the CEN standard require preparation of the fuels prior to the analyses (low temperature ashing at 550 °C) the Simple Slagging Test as well as the Slagging Analyzer are able to analyze the biomass samples as received or in a pelletized form. Although revealing less detailed results than from MAF and CEN, both the Simple Slagging Test and the Slagging Analyzer are able to detect contaminations causing increased slagging in woody biomass samples. Analyses of non woody biomass with high ash content and low ash melting temperatures are on the other hand more uncertain. The Simple Slagging Test is not able to deviate between different samples and reveal all samples except pure wood as slagging. The Slagging Analyzer is able to graduate between the different non-woody biomass samples, but reveals unstable analysis conditions with the high ash containing samples, and does not reveal the same positive effects on contaminations and additives to these fuels as is found with the CEN/TS 15370-1 and the MAF method. **Future works** will thus focus on improving the slagging analyzer and make it more robust also for biomass fuels with high ash contents.

Results from simple salt-ion test and simple salt test methods as well as correlations with chemical index did not reveal correlations with the other melting tests and were thus disregarded in the conclusions from the current investigations. It can, nevertheless, not be excluded that these methodologies could be useful in future investigations. Guidelines for using simple salt-ion test are thus attached as Appendix 6.

The results from the current laboratory methods cannot be used for a direct prediction of slagging and fouling in large scale combustion units as none of these laboratory methods does or can simulate all the conditions that ash and slag is formed at in all the different combustion units and operational conditions used in such units. The laboratory methods can, however, give important insight to the relative behaviour of different types of biomass ash and also to possible effects by

changes in their chemical composition, e.g. by contaminations. The most suitable method depends on the need for detailed information, the time frame for the analyses and the available equipment. Moreover, due to the current lack of information it is suggested that **future works** will focus on correlating results from laboratory methods with operational observations using these fuels at large scale combustion units. It is thus suggested to combine this with a further development of chemical index adapted to Danish combustion plants.

Contaminations of biomass can be an important source for increasing slagging and fouling properties of the biomass by lowering the ash melting temperature, but it can also be a major source of environmental toxic heavy metals. Such contaminants could occur from usage of waste material in the biomass and are very difficult to detect by the naked eye.

Fast chemical analyses for screening biomass fuels for contamination would thus be a strong tool for quality control. The tested XRF analyses, energy dispersive (ED) and wave length dispersive (WD), were both concluded being suitable for such onsite screening analyses for elevated concentrations of heavier elements, e.g. heavy metals. The WD-XRF is the most powerful of these two methods and is able to detect particle emissions consisting of lighter elements such as Na, Mg and Al, while the ED-XRF was concluded less reliable for these elements and thereby also less reliable for detecting particles. Both methods revealed discrepancies for the element Si compared to wet chemical analyses of a parallel sample. The reason for this could not be explained, but it was concluded that in order to be able to further standardize the XRF methods, there is a need for standardized and certified biomass reference material. Such material does currently not exist on the market and it is thus suggested that, in addition to **further works** on standardizing the XRF analyses methods, further works on producing standard materials for relevant biomass samples should be conducted too.

In **WP4.1**, the chemical laboratory method in CEN/TS 15440 for determination of organic carbon in waste material was tested and significantly better results were obtained by using a continuous stirring by a Teflon coated magnet instead of the recommended hand-stirring of the beaker after addition of sulphuric acid. It is therefore recommended that a slow continuous stirring by a Teflon coated magnet is used instead of the recommended thorough stirring at the beginning of the method.

The chemical method in CEN/TS 15440 was tested on a mix of SBR rubber and wood particles and tests showed a significantly higher degree of degradation than was recorded from tests with the individual materials. This is caused by the fact that the heat of reaction from the wood's reaction with the chemicals heats the mixture to a higher temperature than obtained by a reaction of SBR rubber and chemicals. As the rate of reaction is increased with increasing temperatures, materials with a limited degree of conversion, like rubber, will be degraded to a larger extent in mixtures with easily degradable biomass.

In connection with the chemical method in CEN/TS 15440, concentration limits are given for a number of materials in order to obtain an acceptable margin error in the estimation of the biomass content. Based on the observed higher rate of reaction in mixtures it is assumed that the concentration limits given in CEN/TS 15440 may be underestimated for some waste materials.

When using the chemical method in CEN/TS 15440, the waste is grinded to less than 1 mm. If the waste to be tested is based on composite materials with biomass fibres of dimensions less than 1 mm, e.g. cast in plastic polymers/resins with a low degree of degradation, it is assumed that the

method underestimates the biomass content. This effect is expected to be caused by a protecting layer of plastic/resin which will prevent a complete degradation. Attention should be paid on this possible error if the tendency of using composite materials in products is increased.

An alternative laboratory method to the chemical method in CEN/TS 15440 for analyzing the content of biomass in waste, may be an enzymatic method, where enzymes attack specific chemical sites in biomass and liquefies the biomass content of the sample and the rest remains solid. If this goal is obtained in a rather simple way and within a short treatment period (1 day) it will be a suitable method. However, to be a success, it must further be ascertained that the enzymes do not attack polymers based on fossil fuels. A separate **future investigation** is necessary to validate the technical possibilities of an enzymatic method and the advantages/disadvantages by such a method.

In **WP4.2**, results from initial laboratory tests with online NIR analyses of wood pellets clearly identified good possibilities for developing usable NIR spectra models for the parameters' water content, ash content and calorific value, while it was not possible to develop acceptable models for the remaining parameters (trace-element contents, element content and size distribution data). The correlation between measured (reference) values, and predicted (model) values was not satisfactorily good for these parameters. It can, however, not be ruled out that models of these parameters can be successfully made later on, as it was only decided that the models at hand were not good enough.

The following full scale investigations of wood pellets at the Køge Biopillefabrik confirmed the laboratory results on water and calorific value and tests of two different NIR instruments both could analyze water and calorific value with satisfactory accuracy. It was, however, impossible to develop a calibration for ashes. This is due to the relatively small content of ashes in wooden pellets (in relation to the NIR technique) and the small variation in the sample. The investigations at Køge Biopillefabrik showed that it is possible to establish a non-contact online NIR measurement of water and calorific value of wooden pellets above a belt conveyor and both NIR instruments can manage the task tending towards better or more robust calibrations of the MATRIX-F instrument.

**Future works** will focus on further development of the method and installation on more sites and applications where online information on ash and moisture content could be of great value. Such application could be coupling regulation to analyses in feeding systems on straw-fired power plants, regulation at feeding of wood chips at gasification plants as well as process control at pellet productions plants. Several energy companies have shown interest for this type of applications.

## **2. WP1 Sampling of Solid Biomass Fuels**

### **2.1 Aim**

As part of WP1, Sampling, the project has looked at the sampling of two major types of biomass, viz. wood pellets and wood chips. When the project first started, the available literature about biomass sampling was studied, this included Technical Specifications, Solid Bio fuels – Sampling – Part 1: Methods for sampling, CEN/TC 335.

The participants in WP1 under this PSO project do not consider the existing guidelines for biomass sampling, including the Technical Specifications referred to, to be suitable because they do not ensure the sampling of representative samples. To a wide extent, the existing guidelines on biomass sampling are based on methods extracted from other documents about sampling of bulk materials and considerable empirical experience with the properties of biomass in relation to sampling. Quite simply this is not a viable way to develop methods for representative biomass sampling.

Instead, this project is based on the Theory of Sampling (TOS) which addresses the general principles for development of methods for representative sampling of biomass, and indeed of all types of materials (Appendix 1). TOS provides a coherent, consistent description of how to organize and carry out sampling in a manner which can be documented to result in representative samples. In addition, TOS also contains the sampling tools required to set up a sampling scheme that will ensure the desired accuracy of the analysis.

Unfortunately, current awareness of TOS and competence in its use is limited. To compensate for this, this part report includes a detailed section as an introduction to TOS and the fundamental principles of sampling. The authors hope that this section and the practical examples on application of TOS specifically to sampling of wood pellets (section 2) and wood chips (section 3) can serve as a new platform for developing sampling schemes that in a specific setting will ensure representative samples.

The EU has defined as its target to markedly increase the use of biomass as a CO<sub>2</sub> neutral source of energy. The market will see many types of biomass – known and new ones – and the players will need to be able to characterize these by making the right choices in relation to their use. The various types of biomass will have widely different characteristics and properties. It makes no point to imagine that joint guidelines can be developed on how to procure representative samples of such an extensive selection of biomass types. Instead systematic efforts should be invested in expanding the knowledge and understanding of how to use TOS as a tool, which constitutes the foundation of correct, representative sampling. The purpose of WP1 of this PSO project has been to demonstrate how the principles of TOS can be used to develop sampling methods for wood pellets and wood chips. If – as a result of this PSO project – TOS will find future use in the general sampling of biomass and specifically in the development of dedicated CEN standards, this may well be the fulfilment of the most important aim of WP1 of the PSO project.

## 2.2 Work and Results

Various factors are important to ensure representative sampling. This section will address two central factors of any sampling; viz. the dimensionality of the lot and heterogeneity characterization.

TOS works with sampling in all dimensions. In practice 1-D (sampling of biomass in motion) and 3-D (sampling of biomass from stationary piles, stacks, lots, etc.) are the most frequently encountered situations.

Representative sampling requires that **there is equal likelihood of all parts/fragments of the biomass to be sampled**. In relation to biomass a fragment could be the individual wood pellet, a single wood chip or wood dust. When sampling from stationary piles, it is technically difficult to meet these fundamental requirements to sampling since most often the fragments at the bottom of the pile of biomass will not be accessible for sampling purposes at all; this is often met with example of detrimental segregation in very many lots. As a result of this, attempts should be made to the widest possible extent to change a 3-D sampling so that it can be carried out in the form of a 1-D sampling procedure.

As soon as the biomass is in a state of transportation – either free falling from a lorry or a conveyor belt – it is much simpler to achieve correct sampling. In every instance it should be attempted to carry out the sampling procedure with the biomass in motion. Normally, it is quite easy to ensure a representative sampling procedure in such cases. In what is known as a *variogram analysis* it is possible to estimate all types of sampling errors, including sample preparation and analysis errors. These errors all arise from the interaction between the sampling process and the inherent heterogeneity found in all aggregate substances, including wood pellets and wood chips. Knowing these errors (stated as variances), it is possible to estimate the total sampling as well as the analysis error ratio for any sampling scheme for 1-D systems. This makes it possible to organise a sampling scheme which will fully live up to the desired representatively. For a 3-D sampling procedure it is not possible to make a similar, complete analysis of all sampling errors, though some technical solutions are much better than others.

An important aim of this PSO project has been to carry out so-called heterogeneity characterization of wood chips and wood pellets and demonstrate how the data acquired can be used to develop a sampling scheme and to calculate the sampling errors contained in all sampling procedures.

Thus the project has carried out heterogeneity characterization of wood pellets during unloading of ships in the harbours of Fredericia and Kolding as well as at Avedøre Power Plant in Copenhagen. In Fredericia and Kolding increments were sampled from a free falling moving stream during unloading, whereas the increments at the Avedøre Power Plant were sampled in a stopped belt sampling procedure. This means that all three instances involved the preferred 1-D sampling.

In order to obtain a representative increment from a free falling stream of wood pellets, it was necessary to extract quite considerable quantities of increments with a mass between 200 kg and 400 kg per piece. Subsequently, these very large increments were representatively mass reduced in a rotary divider to reach the final analysis sample mass. The mechanical durability of the wood pellets was the recurrent test parameter in all investigations since this is a technically and commercially essential property in wood pellets.

Based on the three sets of data variograms were calculated. A variogram contains all information required to estimate the total sampling error (TSE) for wood pellets, and the uncertainty of the analysis result was calculated for various sampling schemes. This made it possible to choose a sampling scheme that precisely matches the requested accuracy.

There was a clear difference in heterogeneity between a low quality and a high quality wood pellet which affects the reliability of the analysis result. This investigation demonstrated that it is possible to achieve a remarkably low uncertainty of the analysis result if using 1-D sampling and collecting a composite sample containing 20 increments. Based on a sampling scheme of this type it is possible to determine the mechanical durability of a ship load of wood pellets with an overall uncertainty of  $\pm 0.2$  %-points or better.

In the sampling and mass reduction process a systematic, single-sided error can be introduced which will lead to an incorrect analysis result. This will happen when a representative sampling process is not applied. Tests were carried out to determine systematic errors – in a so-called bias test – by the equipment used for mechanical sampling of wood pellets at Avedøre Power Plant. Also the bias of sampling procedures using a spear and grab sampling using a bucket has been characterized.

At Herning Power Plant extensive 3-D heterogeneity characterization of the water content of wood chips has been carried out by examining five randomly selected lorry loads of wood chips. 3-D heterogeneity characterization of water soluble alkali and the trace elements cadmium, copper and zinc in wood chips was also carried out.

The existing equipment for mechanical sampling of wood chips at Herning Power Plant has been tested, this also included bias testing. Finally, preliminary tests of mechanical mass reduction of wood chips have been carried out at Ensted Power Plant using a disc divider.

In order to determine how biomass sampling takes place today in Denmark, selected players within trade, production and use of solid biofuels have been interviewed; three importers, three producers and four end-consumers.

### **2.3 Conclusions**

The project has developed guidelines in how to carry out sampling of wood pellets and wood chips. These guidelines are based on the principles in TOS (Theory of Sampling), which is the foundation for any representative sampling procedure. Consequently, the project deliberately decided against developing still further matrix-specific sampling guidelines, as is for instance exemplified in CEN/TS 14778-1 "Solid bio fuels – Sampling – Part 1: Methods for sampling". This TS uses a biomass classification according to heterogeneity without actually giving a stringent definition hereof. Hence the specification classifies wood chips as a *homogeneous* biomass with a nominal top size  $> 10$  mm. The PSO project carried out a detailed 3-D heterogeneity characterization of wood chips clearly demonstrating, that water content (a core factor of wood chips) is very heterogeneously distributed in wood chips and that this is critical when determining how to organize the sampling.

This report includes an introduction to TOS with a presentation of the fundamental principles of representative sampling. With the aim of making TOS an operational tool for the development of

biomass sampling procedures, the project has developed a set of descriptions providing specific instructions in what measures to take to develop a sampling scheme that lives up to a specific sampling situation. These descriptions are enclosed as Appendix 1.

As an example of how TOS can be used in practice, the project has reviewed sampling of wood pellets during transportation and sampling of wood chips from a stationary container. The first scenario is a 1-D sampling situation involving several advantages. Normally, it is quite simple to ensure representative sampling (i.e. equal chance for all particles of the biomass to be extracted) and it is possible to carry out heterogeneity characterization using the variogram technique. The variogram is a fundamental tool to describe aspects as autocorrelation between increments, calculation of minimum achievable sampling error and calculation of the total sampling error of any sampling scheme.

Sampling from stationary lots belongs to the 3-D sampling regime. In principle it is much more difficult to ensure a representative sample from stationary materials, but there are technical solutions that have proven to work satisfactorily in practice, as clearly demonstrated at the Herning power plant. Compared with 1-D sampling it takes far more resources to carry out 3-D heterogeneity characterization. However, reliable knowledge of the heterogeneity aspects of the biomass is critical since it is the inherent heterogeneity of the biomass which gives rise to all the dominating errors that arise in all sampling procedures. The Theory of Sampling (TOS) delineates all necessary principles for assessing these issues for all lots, at all scales and allows all possible types of sampling procedures to be evaluated on an objective basis.

### **3. WP2 Physical Characterisation of Solid Biomass Fuels**

#### **3.1 Aim**

The aim of *Work Package 2 – Physical Characterizations of Biofuels* is to provide knowledge about physical characterization of solid biofuels. The specific objective of the work carried out in WP2 is to work towards being able to specify pellet-like biofuels appropriately with special attention to the application within dust-firing. The ongoing standardization work includes methods for determination of the size distribution for materials smaller than 3.15 mm, which is extremely relevant to know in fuel pellets, especially within application in dust-firing. In *WP 2.1-Development of method for determination of the particle size distribution in solid biofuels with a nominal size smaller than 3.15 mm* the objective is to examine the existing method for determination of particle sizes smaller than 3.15 mm. The internal particle size distribution of fuel pellets is another important parameter in connection with dust-firing of biofuel, since grinded pellets are used increasingly for firing. In *WP 2.2-Development of method for determination of the particle size distribution in fuel pellets* the purpose is to develop a method for determination of the particle size of the material which the fuel pellets are made of. This means establishment of a suitable method for dissolving the pellets to the particles included, of which the size distribution thereafter is determined with the method chosen in WP 2.1. Finally, the objective of *WP 2.3-Impurities in biofuels* is to attempt developing a method for determination of the content of physical contaminations in biofuels as e.g. earth, sand, metal and plastic. Wood pellets have a quite low content of ash, so here even smaller contamination with sand and earth has a considerable influence on the ash composition with potential unsuccessful significance for the melting conditions of the ash.

Essential and relevant results from WP 2 will be communicated to the continuous development of common European standards for trade with solid biofuels under the European Committee for Standardization (CEN). The contribution can be in the shape of proposals of improvements in existing technical specifications or complete instructions for new or improved methods based on the work in *Work Package 2-Physical Characterizations of Biofuels*. In the present project, the achieved results will however not be applied for elaboration of actual standard proposals, since this is not a matter included in the frames of this project.

## **3.2 Work and results**

### **WP 2.1**

With an increasing consumption of wood pellets in both entire and crushed condition, there is a distinct need for a method determining the size distribution in solid biomass with a nominal particle size smaller than 3.15 mm. In the project, different methods of determination of the size distribution have been examined, such as mechanical sieving, image analysis and mechanical separation in an air flow. For daily use, there should be focus on optimization of a simple and cheap method, and here mechanical sieving will be a natural solution.

Several parameters have influence on the result of a mechanical sieving, for instance throw and frequency, centrifugal force, sieve load and humidity of the sample. The importance of these parameters has been examined for two different kinds of biomass, wood dust and crumbled straw. During these experiments, different combinations of the essential parameters were applied.

The sieving results of the wood dust show a limited variation between the individual sievings, whereas the results from the sievings of the crumbled straw vary considerably. The largest variation in the achieved distributions for the wood dust exists in the sieve having a mesh size of 0.5 mm, after which the variation becomes less significant with both decreasing and increasing mesh sizes (Figure 1). The variation of retained straw on a sieve will be increased unambiguously with increasing mesh sizes for the sieve. The amount of retained straw varies up to approximately 60 percent for a sieve that has a mesh size of 3.15 mm (Figure 2).

## Træsmuld

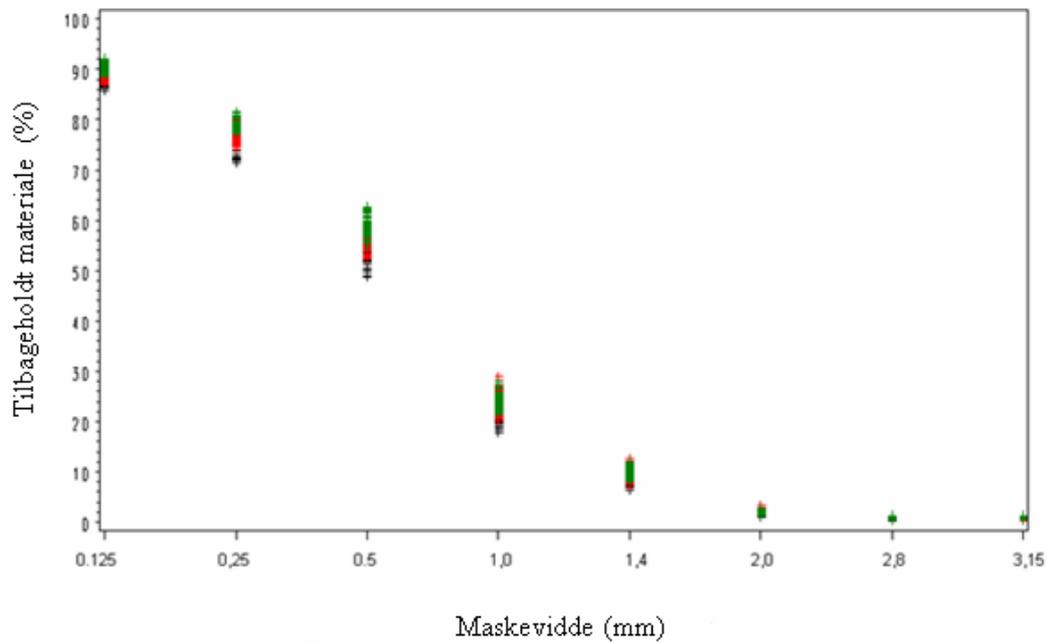


Figure 1: Dispersion of retained wood dust on the different sieves (Black + = DONG; Red + = FORCE; Green + = UoC).  
(Træsmuld... wood powder, Tilbageholdt materiale....retained material; Maskevidde... mesh size)

## Sønderdelt halm

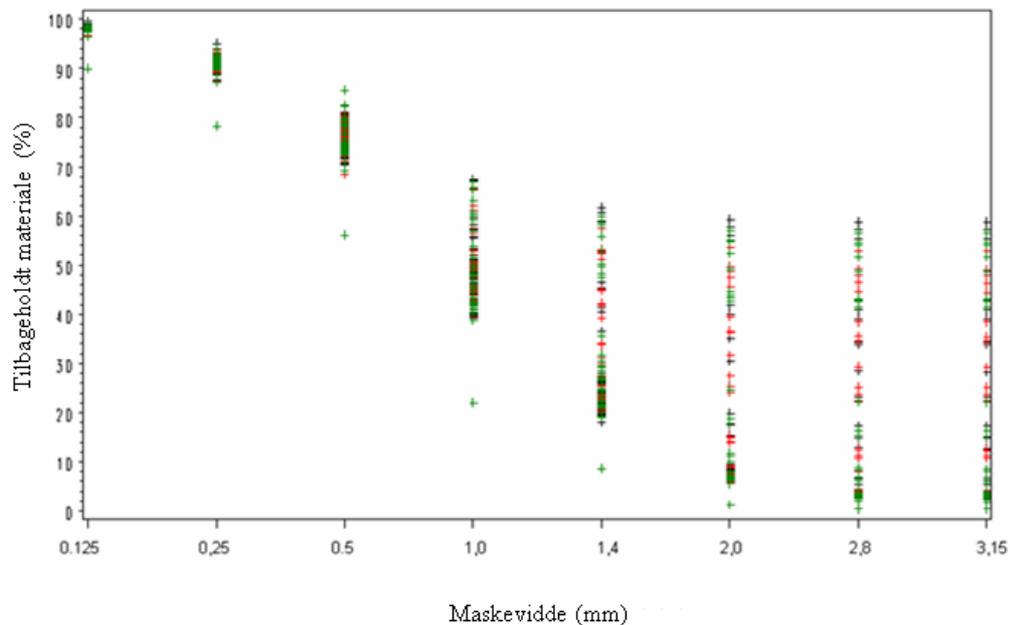


Figure 2: Dispersion for retained straw on the different sieves (Black + = DONG; Red + = FORCE; Green + = UoC).  
(Sønderdelt halm.... Comminuted straw, Tilbageholdt materiale....retained material; Maskevidde... mesh size)

The large dispersion for the distributions of straw is primarily connected with short sieving time and a test amount of 50 g. The statistically diverging distributions have been picked out of the total data set for straw.

For all the distributions of wood and those distributions of straw which do not diverge, 25%, 50% and 75% quantiles are calculated and applied for description of presentation characteristics for the established method. For all fractions from the crumbled straw applies, that there is no significant difference between the individual quantiles, whereas the opposite applies for the quantiles from wood dust. The quantiles have been compared by a single-sided analysis of variance and the result of the analysis has been used for describing repeatability and reproducibility (absolute and relative) of the method (Table 1).

*Table 1: Characteristics for mechanical sieving with sieving tower*

Material	Quantile	$p$	$n$	$X_{mm}$	$s_r$ mm	$s_R$ mm	$S_r$ %	$S_R$ %
Wood dust <sup>1</sup>	25 %	3	72	0.24	0.019	0.12	3.8	24
	50 %	3	72	0.51	0.029	0.16	3.2	18
	75 %	3	72	0.83	0.032	0.091	2.4	6.7
Comminuted straw <sup>2</sup>	25 %	3	40	0.50	0.020	0.032	8.3	13
	50 %	3	40	0.91	0.046	0.021	9.0	4.1
	75 %	3	40	1.35	0.051	0.042	6.1	5.1

<sup>1</sup> Calculations carried out on the complete data set.

<sup>2</sup> Calculations carried out on reduced data set where diverging distributions are omitted.

$p$	Number of participating laboratories
$n$	Number of analysis results
$X$	Average value
$s_r$	Estimation of standard deviation on repeatability level (within laboratories)
$S_r$	Estimation of the relative standard deviation on repeatability level
$s_R$	Estimation of standard deviation on reproducibility level (between laboratories)
$S_R$	Estimation of the relative standard deviation on reproducibility level.

Generally it applies that the relative standard deviation in the results increases with decreasing particle sizes, so that the uncertainty is relatively higher for the small particles than for the more coarse particles. On the contrary, the absolute standard deviation is almost identical for all sieve sizes, and an absolute requirement on precision could be demanded for the method.

The size distribution for the wood dust and the crumbled straw was for mesh sizes smaller than 1.00 mm also examined with Alpine air jet sieving for a comparison with the size distribution obtained with the mechanical sieving in sieving stack. However, it was established that Alpine air jet sieving is not suitable for straw due to the low relative density of the straw.

Regarding the wood dust it was established that the difference in the amount of retained wood dust and hereby the degree of complete sieving, only varies to a limited extent between determinations at the mechanical sieving in sieving stack and determinations with air jet sieve. The results from the air jet sievings are completely identical for the two sieves with the smallest mesh size, whereas there is a smaller difference in the amount of retained material in the 1.0 and 0.5 mm sieves.

The size distribution for the wood dust and the crumbled straw was examined by means of image analysis (Camsizer) and compared with the results for mechanical sieving. From an application-technical point of view (for a particle size distribution), the advantage of an image analysis compared to a mechanical sieving is that it describes the actual number of particles in the different sizes, which is interesting in connection with e.g. dust-firing.

## WP 2.2

Fuel pellets in the shape of straw and wood pellets are increasingly applied for suspension firing in e.g. combined heat and power plants. The pellets are combusted after having been grinded to minor particles in a hammer mill and to obtain optimal combustion it is important to know the particle size distribution in the fuel and, if possible, to ensure that the grinded product has the right particle composition.

In the project, a method has been developed for wet disintegration of fuel pellets and a more fundamental comprehension has been achieved for application-technical aspects of the method which in practice makes it possible to assess the quality of an accomplished analysis. Besides a reproducible determination of the particle size distribution for those particles included in the fuel pellets, an interesting aspect is also the connection between the actual particle size distribution of the raw material, the resulting particle size distribution at dissolution of the pellets and the particle size distribution for the produced fuel flour in a hammer mill. A direct connection between the particle size distribution of dissolved pellets and the particle size distribution for the produced fuel flour will increase the value of those results that are achieved with a wet disintegration as the pellets' suitability for suspension firing can be determined already at the reception.

The present examination consists of three parts, which briefly are mentioned below.

- **PSO5297 Round Robin:** First examination based on the then draft of a CEN standard ("WG 4 Disint. pellets rev20060614"), where a wet disintegration of fuel pellets is used with demineralized water at ambient temperature.
- **CEN WG4 Round Robin:** Second examination carried out in the context of CEN WG4 with participation of six European laboratories experienced in testing of solid biofuels. The examination applies a method developed on the basis of obtained experiences in the PSO5297 Round Robin.
- **Application-technical examination of the method:** Third examination is a comparison of particle size distributions in raw material, wet disintegrated wood pellets and wood pellets grinded in a hammer mill, respectively.

The examinations are carried out on a different range of wood and straw pellets, wood dust, crumbled straw and wood powder from wood pellets divided with hammer mill. All ranges are sampled and divided according to the requirement on equal and representative tests that are necessary if one should be able to carry out comparisons of the obtained results.

As part of the project, a Round Robin was carried out by the three partners of the intermediate project. The purpose of the examination was to find out whether the method described in CEN WG4 Disint. pellets rev20060614, offers comparable results between laboratories, and if even

improved results can be achieved by application of boiling water and stirring of the suspension instead of water at ambient temperature and without stirring.

Dissolution of fuel pellets was carried out with different combinations, both with water at ambient temperature and boiling water and with and without mechanical influence of the suspension. The results from the individual laboratories show that the dissolution becomes more and more complete, when leaving the original CEN method where only water at ambient temperature is used towards using methods with only one supplementary means, to a combined stirring and boiling water. Contrary to dissolution of the straw pellets, the results for dissolution of the wood pellets are far more unambiguous, since the combination of stirring and hot water involved a more complete dissolution than what could be obtained using single means exclusively.

CEN WG4 Round Robin was carried out with six participants. The purpose of the examination was to test the method for wet disintegration of fuel pellets, which was elaborated on the basis of the experiences obtained from PSO 5297 Round Robin, and to assess the quality of the method.

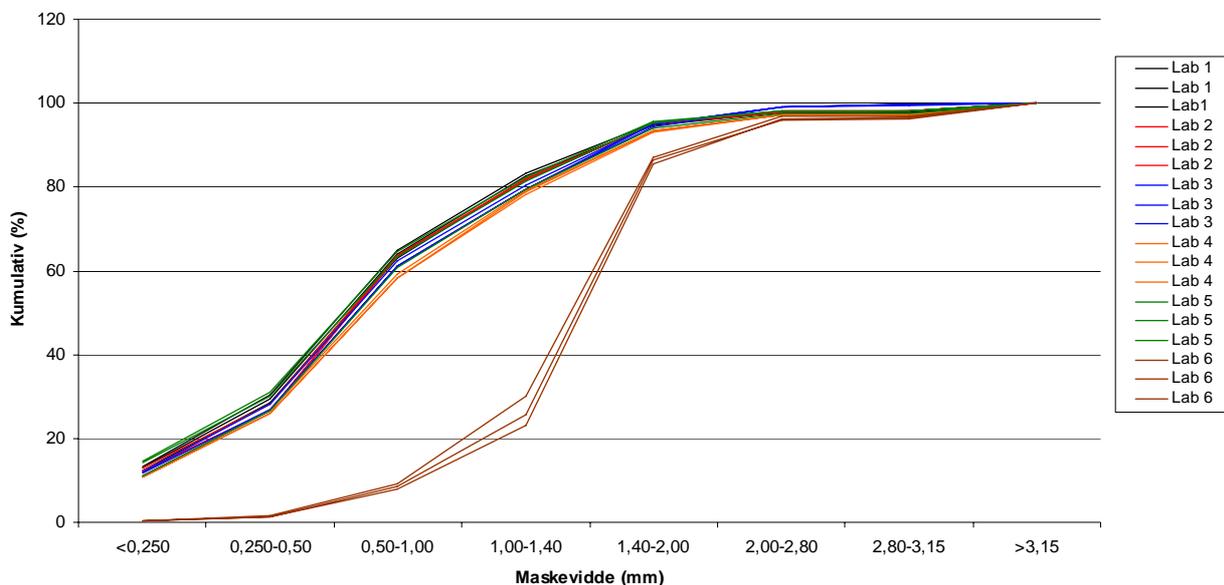


Figure 3: Original particle size distribution in soft wood pellets determined with heated demineralized water and stirring.  
(Kumulativ... cumulative, Maskevidde...mesh size)

The particle size determination was carried out on the basis of the method developed in the WP 2.1 Round Robin. Out of the six participating laboratories, straw pellet results were reported from three laboratories, whereas soft wood pellets and hard wood pellets were reported from all six laboratories (see for instance results for soft wood, Figure 3). Except from a single laboratory which had extremely deviating results for both soft and hard wood pellets the variation between the reported results is limited, which indicates that the developed method is suitable for determination of the particle size distribution in fuel pellets.

On the basis of the results from five of the laboratories, repeatability and reproducibility are calculated for the method. These are – as for the results for the mechanical sieving in WP 2.1 – calculated for the 25%, 50% and 75% quantiles for the obtained size distributions, see Table 2. As

shown in Table 2, the repeatability is in all cases lower than the reproducibility and at the same time the reproducibility and the repeatability is higher for the crumbled straw than for soft wood, whereas the reproducibility for hard wood is higher than for soft wood. Furthermore, Table 2 indicates that the absolute standard deviation on reproducibility level increases with quantile %, i.e. larger dispersion between the laboratories with an increasing mesh size/particle size. On the contrary it is seen that the relative standard deviation on reproducibility level decreases with quantile %.

*Table 2: Performance characteristics for the method*

Material		$N$	$X$ mm	$s_r$ mm	$s_R$ mm	$S_r$ %	$S_R$ %
Soft wood	Quantile						
	25 %	5	0.46	0.018	0.039	3.9	8.5
	50 %	5	0.83	0.016	0.049	1.9	5.9
	75 %	5	1.2	0.018	0.063	1.4	4.9
Hard wood							
	25 %	5	0.33	0.0082	0.055	2.5	17
	50 %	5	0.72	0.016	0.089	2.2	12
	75 %	5	1.3	0.028	0.087	2.1	6.5
Comminuted straw							
	25 %	3	0.46	0.025	0.056	5.5	12
	50 %	3	0.91	0.039	0.067	4.3	7.4
	75 %	3	1.4	0.057	0.092	4.0	6.3

$N$  Number of values

$X$  Average value

$s_r$  Estimation of standard deviation on repeatability level (within laboratories)

$S_r$  Estimation of the relative standard deviation on repeatability level

$s_R$  Estimation of standard deviation on reproducibility level (between laboratories)

$S_R$  Estimation of the relative standard deviation on reproducibility level.

An application-technical examination of the method was carried out by means of inspection of tests of respectively sawdust and wood pellets manufactured of this (Køge) and wood pellets and hammer-grinded wood powder made of the pellets (AVV). The result is shown in Figure 4. The sawdust was tested both directly by dry sieving and by wet disintegration followed by dry sieving.

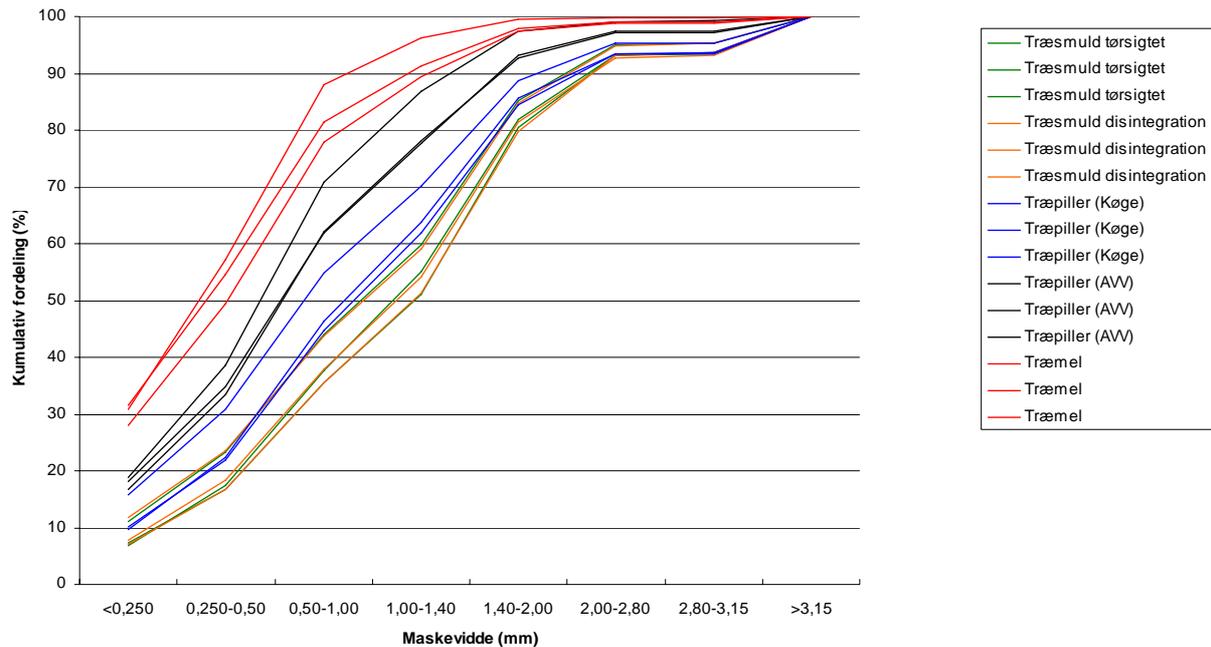


Figure 4: Particle size distribution of wood dust, wood pellets and wood powder, respectively. (Kumulativ fordeling...accumulated distribution, Maskevidde...mesh size, Træsmuld...wood dust, Træpiller...wood pellets., Træmel....wood powder)

By comparison of the results for wood dust, dry-sieved and wood dust, disintegration, it is obvious that these are comparable. Thus, the determined wet disintegration has caused no changes in the particle size distribution of the sawdust.

If the results for sawdust are compared with the results for the wood pellets (Køge), it is found that the wood pellets (after press) have a larger content of fine particles than the belonging wood dust (raw material). This might be due to the fact that wood dust particles are compressed irreversibly or are cut off in the press. However, it cannot be excluded – due to the modest examination – that the sample taken from wood pellets is not totally made of wood dust represented by the sample taken from wood dust.

If the results for wood powder are compared with the results for the wood pellets (AVV) it is found that the wood powder (after hammer mill) has a larger content of fine particles than the pellets. This is very likely due to the fact that the hammer mill on AVV not only disintegrates the pellets to the internal particle size distribution which the pellets have, but additionally disintegrates the particles. However, it cannot be excluded that the sample taken from the wood powder is not totally made of wood pellets represented by the sample taken from wood pellets.

The developed method has proved to be suitably for wet disintegration of the three tested pellet types, soft wood, hard wood and straw pellets, respectively. Since these three types of raw material cover the primary market for commercially available fuel pellets, it can be concluded that the method is well-qualified as basis of a European standard for determination of particle size distribution of fuel pellets. The particle size distribution in pellets obtained by the method will however not necessarily be either the original particle size distribution of the applied raw material or the appeared particle size distribution for produced wood powder from the pellets. However, a

relative connection must be expected to exist, thus the method is applicable for characterization of particle sizes in fuel pellets when used in suspension firing.

### **WP 2.3**

Impurities as e.g. sand, earth, machine parts and similar which have entered into the biofuel due to an inappropriate handling during the production and/or storage, is a well-known quality-reducing factor. Mineral impurities in the raw material for pellet production are for instance caused by inappropriate storage conditions. Mineral impurities in produced pellets can also be due to production conditions. A certain amount of fine impurities of mineral origin is difficult to avoid in e.g. wood chips. Impurities can be caused by inappropriate storage of raw wood at gravel roads, dragging of entire trees above the forest floor, making chips out of forest residues and roots, etc. Metal fragments, plastic parts and similar should under no circumstances be included in any biofuels.

Metal fragments, plastic parts, larger stones and similar can relatively more easily be identified, compared with fine mineral impurities like sand and earth. A simple ashing of the biofuel offers an aim for the total content of ash-forming components. As there can be a rather considerable natural variation in the ash content in biofuels, the ash content will not necessarily on its own be sufficient to determine whether the ash is caused by mineral contamination or just indigenous ash-generating components in the fuel. The indigenous ash-forming connections in biomass vary considerably between different types of biomass, but also within the same type of biomass.

The present examination consists of several parts, which are being described briefly below. The single parts are focussed on coarse impurities with a nominal top size, NTS > 2.0 mm and fine impurities with an NTS < 2.0 mm, respectively:

#### **Generally:**

- Experiments regarding the significance of mineral contamination on ash melting conditions for biofuels.

#### **Coarse impurities (nominal top size > 2 mm):**

- Visual determination of coarse impurities.

#### **Fine impurities (nominal top size < 2 mm):**

- Wet sedimentation of fine impurities.
- Chemical determination of fine impurities in biofuels.
- Identification of added impurities in wood dust with Rationel Frørensner, model MLN.
- Proposal for stepwise determination of impurities, where fine impurities are determined by a combination of horizontal air separation and mechanical sieving. In the proposal, a possible suitable method is described for stepwise determination of the content of impurities in solid biofuels.

In *WP 2.3-Determination of Impurities in Biofuels* a series of examinations were carried out describing different approaches for uncovering the content of impurities. An initial experiment showed that the presence of even small amounts of mineral impurities has influence on the ash melting course for biofuels.

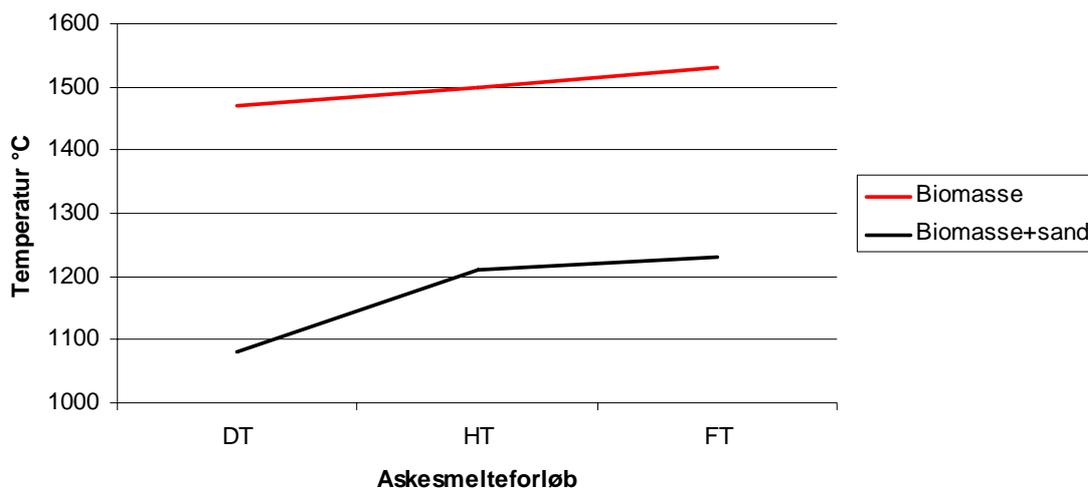


Figure 5: Ash melting course, cf. CEN/TS 15370-1 for pure biomass and biomass with sand added. DT: Softening temperature; HT: Hemisphere temperature; FT: Flow temperature (FT for biomass is measured to >1500 °C but set to 1530 °C to visualize the temperature sequence).

By mixing sand that has a mean grain size of 0.15 mm with a debris portion of wood pellets in an amount corresponding to the ash content in the wood pellets, a considerable deterioration has been found of the ash' melting conditions determined cf. CEN/TS 15370-1. The assumption that sand contaminations can influence on the fuel's ash melting conditions was thereby confirmed (Figure 5).

For determination of coarse impurities a method was elaborated based on mechanical sieving, which subsequently was tested in a mini Round Robin test with two laboratories. The result of the mini Round Robin test which included attempts of re-finding added impurities showed that it is possible to identify and quantify impurities with a nominal top size > 2 mm using the developed method. Subsequently, final instructions for the tested method have been elaborated "Guideline – Solid biofuels – Determination of Visual Recognizable Impurities > 2 mm".

The wet sedimentation, chemical separation and separation in vertical air flow was examined as possible methods to determine the content of fine impurities as sand, gravel and earth particles in solid biofuels. None of the methods showed to be suitable, however. As a result of the examinations, a draft has been carried out with principles for a stepwise determination of particular impurities in primarily wood chips and other wood-based fuels as pellets, patent fuel and straw pellets. Furthermore, a prototype has been designed for determination of the content of fine particular impurities based on a separation in horizontal air flow (second step of the method). Since the prototype was not quite finished by the end of the present project, no testing has been carried out. As the method principle is found to be promising for a determination of the content of fine impurities in solid biofuels, further work within this matter will continue under management of the European project BioNorm II.

### 3.3 Conclusions

In **WP 2.1**, determination of the particle size distribution has been carried out for two biomass types, respectively wood dust and crumbled straw. The size distribution is determined by mechanical sieving in sieving tower, by Alpine air jet sieve and by image analysis in a Camsizer.

Mechanical sieving is a simple and relatively cheap method for control of the size distribution of a material, where one however should be aware of the fact that fractionation takes place basically according to the width of the particles, and that the weight fractions not directly can be related to the number of particles. The image analysis offers more pieces of information such as number and shape of the particles. From an application-technical view (for a particle distribution), the image analysis is also more describing, since it is the number and shape of the particles in the different sizes that are interesting at e.g. dust-firing. Determination with the Alpine air jet sieve did not result in a larger degree of pure sieving, and therefore there is nothing – not even on the basis of the actual examination – to support the choice of air jet sieve as a method for determining the particle size distribution of the smallest particles for biofuels when looking at the degree of pure sieving. Air jet sieving has however other advantages, e.g. in shape of easier cleaning of the sieves after determination.

In **WP 2.2**, a method has been developed for determination of the particle size distribution in fuel pellets. The developed method proves to be suitable for disintegration of the three tested pellet types, respectively hard wood, soft wood and straw pellets. Since these three types of raw material cover the primary market for commercially available fuel pellets, it can be concluded that the method is suitable as basis for a European standard for determination of particle size distribution of fuel pellets.

In **WP 2.3**, a tested method has been elaborated for determination of the content of coarse impurities in biofuels. Wet sedimentation, chemical separation and separation in vertical air flow were aspects examined as possible methods for determining the content of fine impurities as sand, gravel and earth particles. None of these methods proved to be suitable. As result of the examinations, a proposal has been developed as a draft of a principle for a stepwise determination of particular impurities in primarily wood chips and other wood-based fuels such as pellets, patent fuel and straw pellets. For the method principle's step 2 there is designed a prototype of equipment used for determining the fine particular impurities, which will be examined under management of the European project BioNorm II.

As a result of *Work Package 2-Physical Characterizations of Biofuels* the following has been elaborated:

- Essential proposed amendment for the future EN standard for determination of particle size distribution in solid biofuels with a nominal top size less than 3.15 mm, draft CEN/TC 335 N174, 2008-01 Solid Biofuels – Part size distr. 2 (AP2.1).
- Guideline for the Determination of Internal Particle Size of Fuel Pellets (Appendix 2).
- Guideline – Solid biofuels – Determination of Visual Recognisable Impurities > 2 mm (Appendix 3).

- Principle for a stepwise determination of particular impurities in primarily wood chips and other wood-based fuels and design of prototype for determination of fine particular impurities, cf. above.

## **4. WP3 Chemical Characterisation of Solid Biomass Fuels**

### **4.1 Aim**

Slagging in combustion units caused by molten ash is one of the main drawbacks with using biomass fuels, especially when waste biomass fuels originating from industry or agricultural production are used. The problems are caused by typical higher ash content of these fuels but also due to typically lower ash melting temperatures compared to fossil fuels or wood. Presently there are solutions for combusting fuels with lower ash melting temperatures such as e.g. wheat straw, but this has to be adapted specifically to a specific quality of the fuel. This quality does however vary widely between different types of biomass waste and can also vary with season and especially with different handling of the fuel allowing contaminations of soil, dirt or other waste materials.

The present CEN standard for determining ash melting behaviour (CEN/TS 15370-1) was developed from coal ash standards and by some users regarded as insufficient for correct characterisation of biomass fuels. It is thus the aim of WP3 to investigate and test alternative methods for characterizing biomass fuel sample with the main aim to determine potential of slagging. Furthermore, it is also the aim of this work package to investigate methods for fast onsite analyses which are able to find potential contaminations in the biomass causing this slagging.

In Europe there are a number of standards for characterization of biofuels under development. The purpose of these standards is to promote the trade with biofuels on equal conditions in Europe. The long-term purpose of this project is thus to maintain the Danish platform in this perspective and remain being able to propose methods forming the basis for standards for characterization of biofuels. It has therefore also been the aim of this work package to create guidelines for using these new characterization methods that easily can be transformed into eventual new standards for characterizing biomass fuels in the future.

### **4.2 Work and results**

The work of WP3 comprises R&D work for methods for determination of ash melting of biomass fuels and quick methods indicating whether the biofuel is clean or contains contaminations either from other sources such as demolition wood or by bad handling and soil and dirt.

Seven biofuels with known different characteristics were chosen for the purpose of testing the methodologies investigated: debarked wood chips, wood chips from willow (salix), Estonian wood pellets, bark, wheat straw, wheat seeds and rape straw. The samples were milled and all but the debarked wood chips and the willow were also pelletized.

Moreover, in order to investigate the effect and the possibility to detect contamination by new developed methods, mixed pellets of the seven fuels with different amounts of gravel (small and large particle size), fine soil dust and kaolin, added to the milled biofuels prior to the pelletization were also conducted. The amounts added were chosen according to the ash content of the pure biomass. All together 26 samples were produced and investigated (see Table 3).

*Table 3: Origin and explanation of biomass fuel samples chosen for the investigations in WP3, Chemical Characterization.*

Type	Producer and cause of selection	Contaminants/additives (% w/w <sub>dry</sub> )			
		fine gravel	coarse gravel	soil dust	kaolin
Wood chips , debarked	Produced from red spruce by KVL. The sample represents pure wood, which normally does not cause any slagging problems. Thus used as reference.	0,3% 0,6% 1.2 %	0,3%	0,3 %	
Willow chips	Delivered by Ny Vraa Bioenergi. The willow sample represents an energy wood crop, which has different ash properties compared to the common spruce and fur wood.			2 %	
Estonian wood pellets	Provided by DTI from a batch of wood pellets which the customers complained about slagging in their furnaces. This sample does thus represent a wood pellet which appears to be of good quality for the naked eye but shows slagging problems during combustion.				
Bark	Garden bark purchased in a local store. This sample represents bark, which has a much higher content of ash than the core wood.	2,6%	2,6%		
Wheat straw	Local producer at Sdr. Stenderup. Grown on clay soil. The sample represents wheat straw which is known to cause heavy slagging problems.	4,0%	4,0 %	4,0%	4,0%
Wheat kernels	Purchased at local feed stuff stores. The sample represents kernels, which typically also would give slagging problems but which have a different ash chemistry compared to straw.		1,7%	1,7%	1.7%
Rape straw	Local producer at Sdr. Stenderup. Grown on clay soil. The sample represents rape straw which has a different chemical composition compared to wheat straw.		4,0%	4,0%	4,0%

### **Analysis of ash melting and slagging potentials**

The existing standard for ash melting temperatures CEN/TS 15370-1 were conducted for both pure and contaminated biomass fuel samples and used as comparison with the results obtained from the new methods developed in the project.

Three types of ash melting methodologies were investigated and evaluated:

1. the **MAF method**,
2. the “**Slagging Analyser**” and
3. the quick test “**Simple Slagging Test**”.

The **CEN/TS 15370-1** standard originates from coal ash analysis methodology and is performed by first producing an ash of the biomass sample at slow combustion overnight at 550 °C. The remaining ash is then shaped to a cube with sharp edges and stepwise heated in an oven up to 1500 °C. During the increasing temperature, the shape of the ash cube is observed and the temperatures at which it starts to deform due to melting are determined. These deformations are divided into three temperatures where characteristic deformations occur (see Figure 6). The first temperature is the Deformation Temperature (DT) where the sharp edges of the cube are rounded, the second temperature is the Hemispherical Temperature (HT) where the molten ash forms a half ball due to surface tension, and when the ash is completely molten and floats out the Flow Temperature (FT) is finally reached.

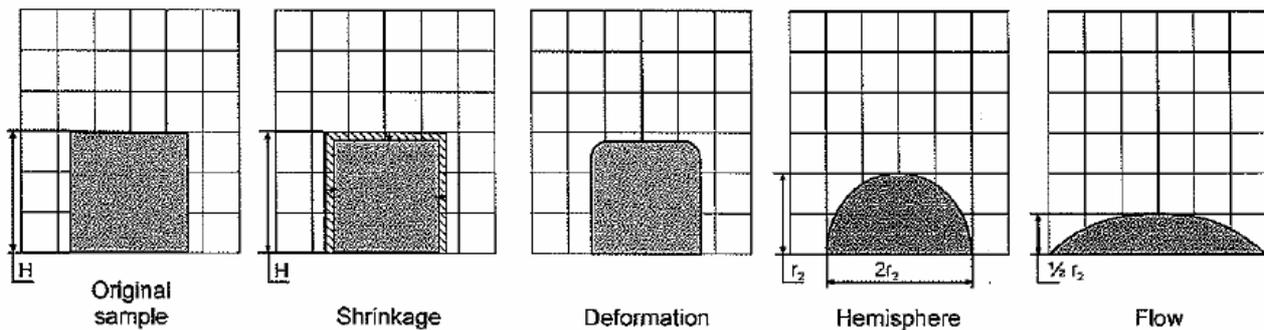


Figure 6: Phases in the ash melting process according to CEN/TS 15370-1 (original shape = shape and size of ash at 550 °C)

The **MAF (Melt Area Fraction)** methodology is based on the following procedure: A milled ash sample (laboratory made from the biofuel at 550 °C) is heated with a controlled heating rate under a microscope. Molten ash particles float out on the hot surface and thereby increase the area shadowing the light through the specimen glass, i.e. the more molten ash the larger is the area covered. This change in area is registered by computer-aided video analysis and a characteristic curve of the melting behavior of the investigated ash sample is generated over the temperature range investigated (Figure 7).

The MAF method differs from the CEN/TS 15370-1 method as it registers the behaviour of the ash gradually over the temperature interval of 500 to 1200 °C and the MAF method can also register inhomogeneous behaviour of different parts of the ash such as separate melting of more than one phase melting at different temperatures, i.e. salt and silicate melts. The CEN/TS method also analyzes the whole temperature range but only registers points on the melting curve such as the DT, HT and FT and it analyzes the whole ash sample as a homogeneous sample.

These two different ways of analyzing the melting behaviour of ash makes the two methods difficult to compare. In order to be able to compare with other methods, three points on the MAF curve, T1, T10 and T50, were chosen as indicative temperatures. These points represent the temperatures at which 1, 10 and 50 % of the solid ash is molten respectively (see diagram in Figure 7).

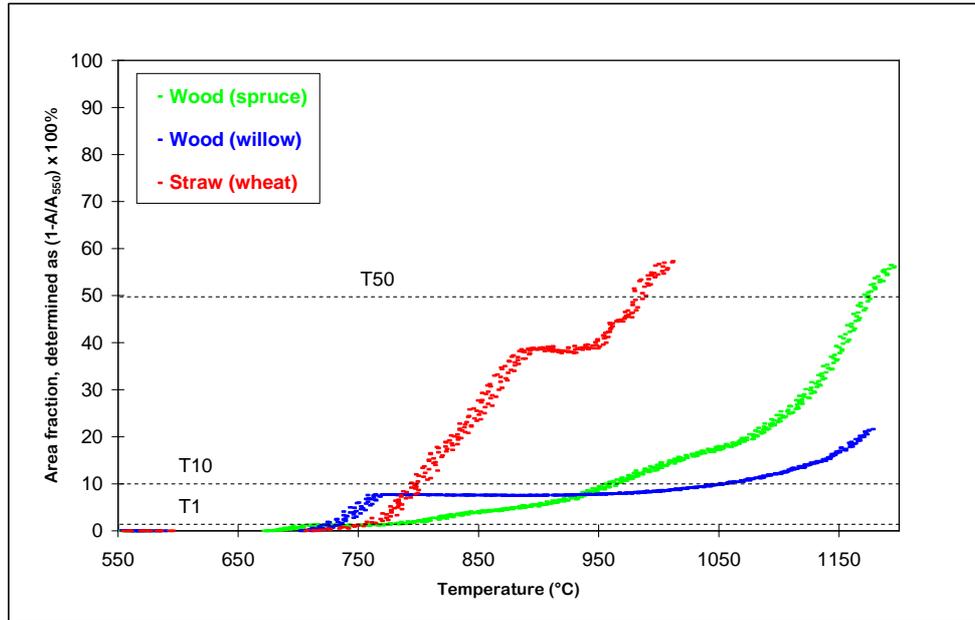


Figure 7: Diagrams with MAF curves, revealing T1, T10 and T50 levels for spruce wood (sample 1), willow wood (sample 2) and wheat straw (sample 5)

The “**Slagging Analyser**” is a small scale, down-fired grate combustor using 2-5 kg of pelletized biofuel. The fuel is combusted under controlled conditions and the remaining ash and slag on the grate is evaluated according to the relative amounts of slag clogging to the grate as well as the size of slag particles by means of sieving analyses (see Figure 8).



Figure 8: Grate with remaining ash and sieved ash and slag-particles ( $> 2.5$  mm) after test in the Slagging Analyser with Estonian wood pellets (sample 3) and wheat straw (sample 5).

The results are evaluated according to 5 categories, where category 1 represents biomass with no slagging tendencies whereas 5 indicate very heavy slagging and molten ash (see Table 4).

Table 4: Definition of categories used in the results of the Slagging Analyser

Category	Explanation	Slagg clogging	Slagg particles	Slagg +	Size of slag
		to grate	$> 2,5$ mm	clogging to	
		Mass % of combusted biomass			[mm]
1	No slagging	$< 0.10$	$< 0.01$	$< 0.22$	$< 6$
2	Slagging tendencies	$< 0.75$	$< 0.75$	$< 1.125$	$< 12$
3	Slagging	$> 1.50$	$< 1.50$	$< 2.25$	$< 30$
4	Severe slagging	$< 3.00$	$< 3.00$	$< 4.50$	$< 90$
5	Very heavy slagging, main part of the ash is molten	$> 3.00$	$> 3.00$	$> 4.50$	$> 90$

The “**Simple Slagging Test**” is designed to be a quick test for indicating the slagging potential of biofuels and can be carried out with standard laboratory equipment and possibly onsite. Fuel pellets are heated to  $1250$  °C in crucible for 30 min. and the condition of the resulting ash is visually assessed after cooling. The result is a simple “Yes” or “No” answer concerning existence of molten ash and thereby potential slagging. Examples of yes and no are shown in Figure 9 and Figure 10.



Figure 9: Example of test result "Yes".

Figure 10: Example of test result "No".

The results from the three methods tested as well as the CEN/TS ash melting method are shown in Table 5.

It is for several reasons difficult to compare and evaluate the results from the different ash melting behaviour methods tested in this project. While the slagging analyzer and the simple slagging tests give straight answers to the slagging potential by more or less subjective evaluations, the less subjective CEN/TS and MAF methods suffer from vague decisions criteria for concluding when a sample is slagging or not. Moreover, the CEN and the MAF methodologies investigate the behaviour of ash produced during low temperatures and very slow heating rates designed to keep the volatile elements such as K, Na and S in the ash. In a real combustion unit the heating ratio during ash formation is much higher and the ash forming elements are fractionated into different ash fractions (bottom and fly-ash), each with its own chemical content and consequently also melting behaviour. Thus, even if the CEN and the MAF methods reveal melting behaviour of an ash samples this is not necessarily the same ash that would melt and cause slagging and fouling in a full scale combustion plant. Considering this, the simple slagging test and the slagging analyzer are thereby closer to analyze the actual ashes that are formed compared to a real combustion as they start with the biomass sample and not the ash. However, the fractionation of ash forming elements in a combustion plant depends not only on the composition of the fuel, but very much on the combustion technology used, e.g. stoker grate or suspension fired combustion. Considering this, none of the analysis methods tested would be able to predict the actual slagging in a real combustion unit and the results from these different analyses should therefore instead be used for showing relative differences in the behaviour of different biomass ashes and also the relative effect of adding contaminants and additive to the biomass fuels (see Table 5).

*Table 5: Results of ash melting analysis  
(n.a....not analysed, A...1 is the least slagging and 5 is the worst slagging, another pure wood pellet sample made of debarked wood was used as reference sample for not slagging fuel)*

Sample		CEN/TS 15370-1			MAF			Slagging Analyser	Simple slag test
Id	Raw materials	DT (°C)	HT (°C)	FT (°C)	T1 (°C)	T10 (°C)	T50 (°C)	1 – 5 <sup>A</sup>	Is slagging?
1	Debarked wood chips	830	> 1500	> 1500	733	964	1170	n.a. (1*)	No
8A	Debark. wood chips +Fine gravel 1:1	1090	1110	1130	804	956	1091	n.a.	Yes
11a	Debark. wood chips +Fine gravel 2:1	1150	1190	1230	877	1029	1161	n.a.	Yes
12a	Debark. wood chips +Fine gravel 4:1	1200	1240	1290	742	888	1018	n.a.	Yes
10A	Debarked wood chips +Soil dust 1:1	1100	1130	1170	891	975	1042	n.a.	Yes
2	Willow chips	830	> 1500	> 1500	726	966	> 1200	n.a.	No
13A	Willow chips + Soil dust 1:1	1170	1210	1310	773	984	1190	n.a.	Yes
3	Estonian wood pellets	1210	1220	1230	748	959	> 1200	2	Yes
4	Bark	1260	1300	1310	935	1101	> 1200	3	Yes
14	Bark + Fine gravel	1220	1230	1320	831	995	1190	4	Yes
15	Bark + Coarse gravels	1190	1220	1320	768	935	1175	4	Yes
5	Wheat straw	870	1090	1310	748	798	980	4	Yes
16	Wheat straw + Fine gravel	950	1290	1330	793	833	1180	5	Yes
18	Wheat straw + Coarse gravel	990	1330	1370	776	819	> 1200	4	Yes
17	Wheat straw + Soil dust	990	1340	1400	752	800	> 1200	5	Yes
23	Wheat straw + Kaolin	1290	1370	> 1500	850	1011	> 1200	5	Yes
6	Wheat kernel	740	940	970	709	751	> 1200	3	Yes
19	Wheat kernels + Coarse gravel	1010	1290	1430	722	771	1105	4	Yes
20	Wheat kernels + Soil dust	1090	1410	1470	710	766	1040	4	Yes
24	Wheat kernels + Kaolin	1010	1370	1390	832	937	1090	4	Yes
7	Rape straw	1280	1470	1480	758	1138	> 1200	2	Yes
21	Rape straw + Coarse gravel	1240	1280	1290	681	719	> 1200	3	Yes
22	Rape straw + Soil dust	1270	1280	1300	696	744	1180	4	Yes
25	Rape straw + Kaolin	1240	1330	1340	886	974	> 1200	4	Yes

It is commonly known that herbaceous fuels such as wheat straw is more challenging to combust compared to woody biomass fuels and increased slagging and fouling at lower temperatures are to be expected when using straw.

From the seven pure biomass fuel samples investigated, the wheat material (kernels and straw) reveals the lowest melting temperatures in the CEN/TS 15370-1, the MAF analyses and also show the severest slagging in the Slagging Analyser test runs. The second worst group is Estonian pellets and bark. The least slagging samples are the debarked wood chips and willow chips, which also are the only samples that do not show any indications of slagging in the Simple Slagging Test. The melting behaviour of rape is different to the other fuels and reveals some unexpected results. Despite its high ash content and high amounts of salt, it proves high ash melting temperatures similar to those found for the debarked wood fuels in CEN/TS 15370-1 and MAF analyses. Somehow contradicting to the other analysis methodologies, the Simple Slagging Test revealed a “yes” for rape straw. This is due to that the simple test does not graduate the results as the other methods does and thus only a tendency to slag turns out as a “yes”. As a consequence of this, the only samples which do not slag in the simple slagging test are the pure debarked wood chips and the willow.

Kaolin has previously been used to prevent slagging of ash with high contents of alkali such as straw, while contaminations such as soil and gravels are known to increase slagging of woody ash. The effect of additives and contaminations was different depending on which of the sample the impurity or the additive was added to. While addition of soil and gravel to the woody biofuels (debarked wood chips, willow and bark), decrease the melting temperature (HT) of these fuels' ashes (and thereby increased their slagging tendency), the melting temperature of wheat seeds and wheat straw increased. In accordance with previous experience the addition of kaolin to wheat seeds and wheat straw significantly increases their ash melting temperatures. In contradiction to these results, the Slagging Analyser revealed more slag particles and molten ash in all experiments with any addition of additives or contaminations compared to the pure fuel. This could be explained by, that although the melting temperature of the ash is increased by the addition of kaolin and thereby less percentage of the ash actually melts, the increased mass of ash turns out negatively in the Slagging Analyser's evaluation system as it is based on amount of molten particles larger than a certain size.

The behaviour of rape straw is different from the other samples and reveals that any addition of impurities or additives decreases the melting temperature of the rape ash. This is also in accordance with the results of the Slagging Analyser which revealed a higher slagging category with any kind of addition to the fuel.

### **Online analyses of contaminants**

To detect contamination of biofuels is very difficult, and most of the time impossible, with the naked eye. This is especially difficult if the material is pelletized. The effects of contamination are thus often detected first after it is combusted and ash starts to melt in the combustion unit. Consequently, there is a need for methods which quickly onsite can detect possible contamination in the fuel. XRF techniques have developed rapidly during the last years and are now able to analyze down to ppm levels. The advantage of XRF compared to wet chemical analyses is that there is no need for digesting the sample and the XRF spectra are able to detect a large number of elements at the same time.

In the project two different types of XRF equipment were tested for the purpose of quickly characterizing the fuel for its ash composition and to detect possible inorganic contamination. ED-XRF (Energy Dispersive) was used by FORCE technology and WD-XRF (Wave length Dispersive) by Danish Technological Institute. Comparing these technologies, the WD-XRF was the most powerful and delivers good results for almost all relevant ash forming elements. The ED-XRF, which is less powerful but faster than the WD-XRF, delivers less accurate values for the lighter elements such as Na, Mg, Al in samples with lower concentrations of ash such as pure wood (ash content < 0,5 wt%).

Both methods reveal good and comparable results for heavier elements, e.g. heavy metals, but reveal large deviation in analysis results of Si compared to wet chemical analyses but also compared to each other. This is especially noticeable in the analyses of wheat straw and rape straw samples where Si is the dominating ash forming element. This deviation could not be explained from these analyses and needs further investigations in the future.

Particle contaminations of sand gravel were sufficiently detected with WD-XRF in all samples while ED-XRF was only able to detect particle contamination in the non-wood materials, i.e.

samples with large ash content. The reason for this could not be explained from these investigations.

Moreover, the results revealed that none of the two XRF methodologies are sensitive to moisture content in the samples. Due to the fact that XRF is a surface detection and the surface of the sample dries during the analysis, the analyses results are on dry basis and directly comparable. This fact means that no drying of the samples is required prior to the analyses which significantly improve the speed of the analysis time.

Accordingly, both the ED-XRF and the WD-XRF are well suited for quick onsite screening quality analyses of solid biomass fuels, especially in order to detect contamination of heavier elements such as heavy metals in the fuels.

The WD-XRF is also suitable for detecting particle contaminants such as sand and gravels, while the ED-XRF is less reliable for such purpose. Due to the fact that Si is a major element of slag from biomass fuels, the determination of this element should be improved further, before the results can be used for any slagging predictions.

### **Other alternative methods**

In addition to the above discussed methods, two other methodologies for relatively simple and onsite investigation of chemical characterization of the biomass quality were investigated. The idea was to try to base these methods on standard laboratory equipment instead of more expensive analysis equipment such as e.g. XRF. These methodologies comprise the “**Simple salt test**” and the “**Simple Salt-ion test**”.

The idea of the “**Simple salt test**” was to measure the conductivity changes in water extract from the fine milled biofuels. Water soluble minerals (salts) dissolve from the fuel and subsequently increase the conductivity of the solution proportionally. High amounts of soluble salts would in most biomass samples indicate large amounts of alkalisalts, such as KCl and NaCl and K<sub>2</sub>SO<sub>4</sub>, and these salts are known to increase potential slagging and fouling. The results revealed that the test was successful in detecting high amounts of salts in the samples; however there could not be found any correlations to the melting behavior of the ashes analyzed by the other dedicated methods. This method was therefore rejected as not suitable for characterizing biofuels’ slagging behaviour.

The scheme with the “**Simple Salt –Ion test**”, was to find by simple chemical quick test to detect high and low concentrations of relevant ash-melting elements (K, Na, S, P and Si) and N in the biofuels. Simple chemical test for K, Na, S and Cl were found and tested but no suitable test for Si, P and N could be found. The results revealed acceptable values but due to the lack of results for Si and P no correlations with ash melting behaviours or contamination levels were attempted.

As part of the basic characterization traditional wet chemical analyses were conducted for inorganic content (ash composition) of the biofuels and the contaminants at the start of the project. These values were used as comparison for the other analyses and also used for designing and calculating the chemical composition of the mixed samples.

Investigations using **Chemical Index** of the slagging potentials were conducted based on the elemental concentrations of ash forming elements in the biomass samples investigated. The Index

which is basically value for the relation of elements in the fuels is calculated and compared with slagging and non-slagging ranges defined by previous research carried out on Swedish biomass combustion plants. These ranges are basically set by combining chemical knowledge of molten silicate glass and salt mixtures with experience values of slagging and fouling properties from real combustion units.

Due to the fact that this project did not include any experience from Danish combustion units using the investigated fuels, the chemical index from Swedish combustion units using woody biomass had to be used. The results revealed, however, no or little correlation with the results from the other melting tests.

### 4.3 Conclusions

#### **Methods for analysis of ash melting and the effect of contamination**

Both the **MAF** method and the **CEN/TS 15370-1** method are based on the heating of ash from a biomass sample slowly combusted at laboratory conditions avoiding loss of more volatile elements. I.e. the analyzed melting behaviour represents the composition of the total ash of the biomass tested. In a real combustion unit ashes fractionate and the composition of ash fractions' slagging and fouling in full scale combustion units does not have the same composition as the total ash. Typically fly ashes contain higher concentrations of volatile elements such as K, Na, Cl and S which causes fouling on the convective surfaces of the boilers, while the bottom ash that cause slagging on furnace walls mainly consist of less volatile silicates. Consequently, none of these ashes necessarily resemble the ash composition actually tested by the CEN-TS and the MAF analyses. Considering this, none of these laboratory methods can thereby deliver precise prediction of what temperatures should be used in a combustion unit to avoid slagging and fouling. However, they are both very suitable for a relative comparison and characterisation of the behaviour of the ash from different biomass fuels. Mainly because they deliver reproducible results affected solely by the composition of the ash and disregard the effects of the technology or operation at the combustion plant. These methods are thus also especially suitable to investigate potential relative effects of changing the chemical composition in these fuels with suitable additives. In such cases, the MAF analyses have an extra advantage compared to the CEN-TS method as it delivers more information on the behaviour of the ash during the melting enabling the detection of more than one melting phase in the ash. Consequently, by studying the MAF curves, it can be suggested that the positive effects of impurities and additives to fuels with high salt content such as the wheat materials could shift the dominating melting phase from a low temperature melting salt phase to a silicate phase, which melts at higher temperatures.

Currently, there is only one MAF equipment existing and also only one user of MAF (FORCE Technology). Thus, with the hope of further dissemination and development of this very interesting analysis method a set of guidelines for analyses by means of MAF are included as Appendix 4 to this report.

The **Slagging Analyser** is using pelletized biomass samples and thus the disadvantage of preparing a laboratory manufactured ash is not of importance for this method. In this method the investigated ashes are formed under combustion conditions, although the combustion technology used in this

laboratory equipment is a downfired grate that is not used in any full scale units. In contrast to MAF and CEN a fractionation of ash do occur in the test runs with the slagging analyser, but due to the downfired technology and batch operation, the retention time of the bottom ash on the grate is much longer than is realistic for a real scale combustion unit. Consequently, also this method has to be seen as a reproducible laboratory method that can be used to indicate changes in the ash melting behaviour of the biofuels and not as a simulation of a full scale combustion at a power plant. Considering this, the developed methodology with 5 quality categories was concluded to show repeatable results, and by basing these categories on weighing and sieving of slaggs and ashes after each test run, a fast and fairly objective method for determining potential slagging has been created.

For fuels with low ash content such as wood pellets the Slagging Analyser method has revealed high sensitivity and would be well-suited as a standard analysis for such fuels. However, for fuels with high ash content the method is currently less successful as the high amount of ash blocks the grate and hinders the combustion. Further development is thus necessary in order to be able to characterize the slagging of such fuels with this method in the future. This is the reason why no guidelines were made for the Slagging Analyser.

The **Simple Slagging Test** is based on formations of ash under high temperature and oxidizing atmosphere in an open crucible. Consequently, parts of volatile ash fractions are most likely to escape during the combustion and melting of the ash as it does in a real combustion. However, as concluded for the Slagging Analyser, this method does not simulate the combustion at a full scale combustion plant and the result should be used for relative comparison, too.

The method is very simple and the results are reasonably consistent with those from other melting analyses, although much less graduated. The test which simply determines “slagging” or “no slagging”, is able to separate between pure wood with no slagging and all the other samples which all showed slagging (see Table 5). The method is concluded to be especially suitable for simple quality check of good quality wood pellets, which normally do not slag, but with the slightest contamination would.

Consequently, a guideline for carrying out the Simple Slagging Test is included as Appendix 5 to this report.

The agreement of the different ash melting and slagging analysis methods investigated is in general good for the 7 pure biomass samples and identification of samples with potentially slagging ash is detected by all methods. For the test with added contaminants the results from the MAF and the CEN/TS 15370-1 method reveal similar trends, where contamination of the woody biomass fuels (bark, wood chips and willow) decreases the melting temperature, while contamination and additive to wheat straw and kernel increases the melting temperature. The Slagging Analyser does here reveal another trend and suggest increased slagging of all addition of contaminants or additive to also to wheat straw and kernels.

Which method is the most accurate for predicting the ash melting behaviour and slagging in a combustion unit, cannot be concluded from these investigations alone as none of these methods correctly simulate the conditions that ash is formed and melted in a full scale combustion unit. Baring in mind the very different conditions existing in different types of combustion technologies e.g. suspension fired, fluidised bed or combustion on a grate, it would not be feasible to have one laboratory method simulating all these technologies. The investigated methods should thus be

regarded as laboratory methods, where the relative effects of the chemical composition of the biomass fuels are compared. The use of these values for predicting slagging in full scale combustion units would thus have to be performed by testing the currently used fuels in the specific unit investigated and the new biomass fuel with the laboratory methods and draw the conclusions from their relatively different results. More research on the correlations between laboratory tests and real scale slagging is thus needed in the future.

### **Other alternative methods for chemical characterization and detection of impurities**

The **Simple Salt Test** which focuses on detecting amounts of water soluble salts in biomass by measuring the conductivity of a specified water solution revealed that the test is successful in the detection of content of salt in the biomass samples. However, as there could not be found any correlations to the ash melting behavior detected by the other dedicated ash melting methods, this method was concluded as not relevant for characterizing the slagging potential of biofuels.

The **Simple Salt-Ion Test** was successful in finding fast and simple qualitative analysis methods for obtaining a measure of level of important elements Cl, K, Na, and S in biofuels. No simple methods were found for P, Si and N in the biofuels, but the results from the other elements could be relevant for fast inexpensive part evaluations of biomass fuels. Due to this the guideline in Appendix 6 only includes simple methods for carrying out analyses of the elements Cl, Na, K and S.

The investigations with **Chemical Index** based on values from Swedish wood-based biomass combustion units did not reveal correlations with the other analyses conducted on the melting of ash. Future work should thus focus collection and comparison with operational experience data from Danish combustion units using other fuels than woody biomass for further investigations and development of these indexes.

### **Online analyses of quality and detection of contamination**

Both **XRF** methods (ED and WD) were successfully tested on biomass samples and both methods delivered fast and reliable results on a dry basis for large part of the ash forming elements. Heavy trace elements were also successfully analysed in samples with elevated concentrations.

The **WD-XRF** is the most powerful methodology of the two and was concluded to be very suitable for fast screening analysis of solid biofuels and contaminants such as soil particles or heavy trace elements, e.g. heavy metals from waste wood were effectively detected. However, while the method is good at detecting changes in the fuel, the absolute concentration values of Si can deviate significantly from those detected by wet chemical analyses of the same samples.

The analyses with **ED-XRF** reveal similar results as with WD-XRF but have limitations in the detection of lighter elements, such as Al, Na and Si in fuels with lower ash content such as woody material. The deviations in analysing Si are higher using ED-XRF and do in some samples not detect the known changes in Si at all. This was confirmed with results from traditional wet chemical analyses of the main ash forming elements. ED-XRF is therefore, in contradiction to WD-XRF, concluded not suitable for screening detections of particulate contamination such as stone and dirt in biofuels.

No wet chemical analyses of heavy metals were conducted in this project, but such analyses have been performed in a previous BIONORM project. XRF analyses of the this samples revealed that both WD-XRF and Ed-XRF are able to detect samples with elevated concentrations of heavy metals but that biomass with normal levels were below the detection limit of the XRF methods.

Considering this it can be concluded that both methods are well-suited for fast screening analyses of solid biofuels for the detection of any contamination by heavy metals while the WD-XRF is also suitable for the detection of particulate contaminations of pure sand or dirt.

In accordance with these conclusions, guidelines for carrying out analyses by means of WD-XRF and ED-XRF are included in Appendix 7.

### **General conclusions**

In this project several new methods for characterizing solid biofuels were developed and tested, especially with the focus on ash melting behaviour. Some of these are well-suited for characterizing biofuels and could form the basis for future standards. Guidelines for the use of MAF (Appendix 4), simple slagging test (Appendix 5), simple salt-ion test (Appendix 6) and XRF (Appendix 7) have been produced and are enclosed in this report.

In order to really reveal the value of these new methods they would have to be tested and valid against experience of slagging and fouling in real scale combustion units. The correlations would have to consider combustion technology, local temperatures and atmosphere in the combustion plants where slagging is found. It is first by conducting such comparison the full usability of these methods and their ability to predict slagging in the future can be revealed.

## **5. WP4.1 Biological Origin and Biodegradability**

### **5.1 Aim**

The aim of this work package was to investigate methods for analyzing the biomass content in waste derived fuel in order to account for the CO<sub>2</sub> emission from use of the waste in energy-consuming and energy-producing plants.

### **5.2 Work and results**

According to the Kyoto protocol, energy-producing and energy-consuming plants larger than 20 MW must keep records of their CO<sub>2</sub> emission. If waste derived fuel is used it is necessary to know the part of the fuel which originates from biomass, as this part is considered CO<sub>2</sub> neutral.

This project investigates the present status of methods for analysis of the biomass content of waste derived fuel.

During the project technical specifications have been published for analyzing and calculating the biomass part of waste derived fuel.

One of the methods is described in the specification CEN/TS 15440 and is based on chemical degradation of the biomass content using a rather simple laboratory method, which can be used in the company laboratories. However, the error in the estimated biomass content is significant for a number of waste materials. An example is polyurethane waste which by the method is characterized as nearly 100% degradable and thus classifies the waste to biomass although it is based on fossil fuels.

The biomass part can also be analyzed using a  $^{14}\text{C}$  (carbon-14) based reference method. Advantages and disadvantages of the two methods are being discussed.

As an example, the error in estimating the biomass part by the chemical degradation method is assessed for household waste added to Danish incineration plants based on collected data for the waste composition in Denmark.

Finally, the possibility of developing methods based on enzymatic degradation is studied.

### **5.3 Conclusions**

A test with the chemical laboratory method in CEN/TS 15440 showed a better result by using continuous stirring by Teflon coated magnet instead of the recommended hand-stirring of the beaker after addition of sulphuric acid. The result is caused by an improved contact between liquid and solid for the main part of the time the sample is in contact with the chemicals. By using continuous stirring at a specified rpm instead of thorough stirring, it is avoided that particles are deposited on the walls of the flask. This effect was observed for rubber particles as well as for wood particles. It is therefore recommended that a slow continuous stirring by a Teflon coated magnet is used instead of the recommended thorough stirring at the beginning.

The chemical method in CEN/TS 15440 was tested on a mix of SBR rubber and wood particles. The test showed a significantly higher degree of degradation than was recorded from tests with the individual materials. This is caused by the fact that the heat of reaction from the wood's reaction with the chemicals heats the mixture to a higher temperature than obtained by a reaction of SBR rubber and chemicals. As the rate of reaction is increased with increasing temperatures, materials with a limited degree of conversion, like rubber, will be degraded to a larger extent in mixtures with easily degradable biomass. In connection with the chemical method in CEN/TS 15440, concentration limits are given for a number of materials in order to obtain an acceptable margin error in the estimation of the biomass content. Based on the observed higher rate of reaction in mixtures it is assumed that the concentration limits given in CEN/TS 15440 may be underestimated for some waste materials.

When using the chemical method in CEN/TS 15440, the waste is grinded to less than 1 mm. If the waste to be tested is based on composite materials with biomass fibres of dimensions less than 1 mm e.g. cast in plastic polymers/resins with a low degree of degradation, it is assumed that the method underestimates the biomass content. This effect is expected to be caused by a protecting layer of plastic/resin which will prevent a complete degradation. Attention should be paid on this possible error if the tendency of using composite materials in products is increased.

An alternative laboratory method to the chemical method in CEN/TS 15440 for analyzing the content of biomass may be an enzymatic method, where enzymes attack specific chemical sites in biomass in order to obtain a liquid fraction of the biomass content in a waste mixture. If this goal is obtained in a rather simple way and within a short treatment period (1 day) it will be a suitable method. To be a success, it must further be ascertained that the enzymes do not attack polymers based on fossil fuels. A separate investigation is necessary to validate the technical possibilities of an enzymatic method and the advantages/disadvantages by such a method.

## **6. WP4.2 Characterisation with NIR Analyses**

### **6.1 Introduction and Aim**

Near infrared spectroscopy (NIR) is a spectroscopic method utilizing the near infrared region of the electromagnetic spectrum (from approx. 800 nm to 2500 nm). The molecular overtone and combination bands seen in the NIR are typically very broad, leading to complex NIR absorption spectra. Because of this it can be difficult to assign specific features in the spectrum to specific chemical components. Multivariate calibration techniques (such as partial least squares regression) are therefore needed in order to extract useful information from the NIR spectra. Careful selection of calibration samples and multivariate calibration techniques are thus essential for NIR analytical methods. Today, the NIR technique is among others applied for determination of e.g. water, fat, protein and starch in foods and feeds. The technique is also established in the chemical as well as the pharmaceutical industries.

The NIR light penetrates from less than one mm to several cm into the sample and hence it is often possible to measure directly on a sample without any sample preparation; i.e. it is possible, by using fibre-optic technology, to measure on a product directly in the process line. Thus you can obtain real time information on the product composition in the production phase. Subsequently, this information can serve as input to the process control.

This part of the project aims at investigating and documenting the potential of utilizing online NIR for determination of the quality parameters: Water, ash and calorific value of wood pellets. After the first positive laboratory results the project was extended also to undertake an introductory examination of the possibilities of using NIR for all interesting quality parameters and for demonstration of online NIR in full-scale.

The project has been divided into the following phases which also characterize the formulation of the report.

- Laboratory examinations of the potential of the NIR technique for determination of:
  - water, ash and calorific value
  - density, colour and mechanical stability
  - trace elements and fundamental analyses
  - grain size distribution
- Online NIR full-scale test with water, ash and calorific value.

The results are compiled in a Technical Report as Appendix 8.

A Technical Report is considered as a Pre-Guideline.

## 6.2 Work and Results

Prior to implementing a quantitative or qualitative model at a full-scale production or transport unit, it is beneficial to perform thorough laboratory tests of the potential of the method(s). The tests should, to the largest feasible extent, simulate the real-world scenario, for which the final methods are intended, in order to identify and possibly correct errors and problems. In the laboratories of Aalborg University Esbjerg an equipment simulating the scenario of a moving conveyor belt, was produced. As the sample amount was relatively small (app. 2 kg), and the method involves acquisition of several spectra over a period of time (spectra subsequently averaged), it was necessary that this equipment was “circular” so that the same material passed the measuring point of the spectrometer several times. The speed of the device was app. 1 meter pr. second, simulating the true production situation rather closely. The used spectrometer was a BOMEM MB 160 FT NIR, normally used in laboratories, not (harsh) production environments. A variety of wooden pellet samples was analyzed, in order to achieve a relatively large variation in the measured parameters. The acquired spectra were subsequently related by chemometric (multivariate) models to a set of measured reference parameters (water content, ash content, calorific value, trace element content, content of basic elements (C, H and N), and particle size distribution of broken pellets). As the models turned out to be able to predict the content of some of the parameters (water content, ash content and calorific value) successfully, it was decided to continue the project, and move on towards online implementation, by testing a set of equipment better suited for installation in production, or outdoor, environments.

A non-contact on-line NIR measurement on wooden pellets has been developed based on a measuring head from Bruker Optics and two different NIR instruments: MATRIX-F – a FT-NIR instrument from Bruker Optics with possibility of connecting 6 measuring points to one instrument. This is an expensive solution. The other instrument: NIR 1.7 from Boehringer Ingelheim microParts is a low-cost diode array instrument with one measuring point per instrument.

Initially, the instruments were established in the laboratories of the Danish Technological Institute where a preliminary investigation was performed. Subsequently, the equipment was installed above a belt conveyor after a silo at Køge Biopillefabrik.

Reference samples were taken regularly for analysis of water content, calorific value and ashes for the control and further development of the NIR calibrations. The calibrations were currently developed and the functionality of the NIR instruments evaluated.

The online NIR full-scale test was divided into the following phases:

- 1) Offline NIR measurements at the laboratories of the Danish Technological Institute with subsequent data treatment / calibration
- 2) Mounting of instruments at Køge Biopillefabrik and establishment of web monitoring
- 3) First online calibrations (water)
- 4) Final online calibrations and conclusion.

### 6.3 Conclusions

The initial laboratory tests identified a possibility for developing NIR spectra models of water content, ash content and calorific value on wood pellets by using the BOMEM BM 160 FT NIR instrument and the equipment simulating a moving conveyor belt. It was expected that the modelling success could be repeated on another instrument, also in a full scale production situation where pellets are transported by a real conveyor belt. This was the foundation of the continuance of the project. Unfortunately, it was not possible to develop acceptable models for the remaining parameters (trace-element contents, element content and size distribution data), as the models did not display acceptable correlation between measured (reference) values, and predicted (model) values. It cannot be ruled out that models of these parameters can be successfully made later on, as it was only decided that the models at hand were not good enough. It was further noted that the models at hand were developed on NIR spectra of 2 kg material, whereas the reference analyses were made on significantly smaller portions of material, extracted from the 2 kg. The detailed results and models can be seen in the report, as they are not directly relevant for the final project conclusions, as the goal was to develop full-scale online models.

The introductory investigations of the online NIR equipment at the Danish Technological Institute indicated that it is possible to develop calibrations for both instruments as regards water, calorific value and ashes.

The following investigations at Køge Biopillefabrik confirmed the laboratory results on water and calorific value. Both NIR instruments could analyze water with a RMSEP of approx. 0.4 ranging from 5.2 to 11.3 %. It was possible to analyze the calorific value with both NIR instruments, MATRIX-F being the best with a RMSEP of approx. 0.09 ranging from 15.9 to 17.1 units. It was, however, impossible to develop a calibration for ashes. This is due to the relatively small content of ashes in wooden pellets (in relation to the NIR technique) and the small variation in the sample. The investigations at Køge Biopillefabrik showed that it is possible to establish a non-contact online NIR measurement of water and calorific value of wooden pellets above a belt conveyor. Both NIR instruments can manage the task tending towards better or more robust calibrations of the MATRIX-F instrument.

**Future works** should focus on further development of the method and installation on more sites and applications where online information on ash and moisture content could be of great value. Such application could be coupling regulation to analyses in feeding systems on straw-fired power plants, regulation at feeding of wood chips at gasification plants as well as process control at pellet productions plants. Interest has been shown from several energy companies for this type of applications.

**Appendix 1: Detailed instructions for sampling of solid biomass fuels**

**Appendix 2: Guideline for the determination of internal particle size of fuel pellets**

**Appendix 3: Guideline. Determination of visual recognisable impurities > 2 mm**

**Appendix 4: Guideline for ash melting behaviour by MAF**

**Appendix 5: Guideline for simple slagging test**

**Appendix 6: Guideline for simple salt-ion tests**

**Appendix 7: Guideline for analyses by means of XRF**

**Appendix 8: Technical report NIR**