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# IEA Bioenergy Task 32 project

## Advanced characterisation methods for solid biomass fuels



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## **Advanced characterisation methods for solid biomass fuels**

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## Abstract

Biomass fuel characterisation is a relevant issue for all thermo-chemical conversion technologies. Within the last years several national and international projects were initiated, which focus on advanced biomass fuel characterisation techniques in order to define the behaviour of a fuel during the pyrolysis, gasification and combustion stage as good as possible and thus support the proper design of a conversion plant. These advanced fuel characterisation methods have their specific advantages and application range. Therefore, this study has been performed in order to gain an overview about advanced biomass fuel characterisation techniques presently applied, to discuss the strengths and weaknesses of the different methods, their specific fields of application as well as to assess the suitability of the different methods for the investigation of new biomass fuels.

A comprehensive questionnaire regarding advanced biomass fuel characterisation methods has been worked out and distributed to different organisations active in this field. In total feedback from 22 organisations has been received. Based on this feedback and on information and experiences gained from other European projects (EU FP7 and ERA-NET Bioenergy), a summary and evaluation of different advanced fuel characterisation methods has been made. The advanced methods concerned are thermogravimetric analyses (TGA), fuel indexes, chemical fractionation, scanning electron microscopy and energy dispersive x-ray spectrometry (SEM/EDX), differential scanning calorimetry (TGA/DSC), thermodynamic equilibrium calculations (TEC) as well as test runs at batch and continuously working reactors.

The evaluation of the questionnaires has revealed that obviously no commonly accepted strategy for the use of advanced biomass fuel characterisation exists. Most institutions apply a number of different methods and decide from case to case depending on the fuel and the targeted application which tools they are going to apply. The methods investigated show significant differences in terms of time demand, need for experienced and especially trained personnel, market availability of the hardware and software needed to apply the method, information depth gained and applicability of the results with respect to real-scale process design. Generally, with increasing complexity of the method the information depth gained and the applicability of the data to real-scale processes increases. With this increase of information depth unfortunately also the costs and the time demand for the tests increase, as well as the need for experienced staff to perform the fuel characterisation and the evaluation work.

Based on the evaluations performed it can be recommended to apply the evaluation of fuel indexes as a first step in fuel characterisation in order to gain a qualitative pre-evaluation of conversion related problems to be expected when utilising a specific fuel.

In a second step, test runs at batchwise or continuously operated lab-scale reactors are recommended in order to gain quantitative data. The selection of the reactor, the test run setup and the measurement and analyses program has to be adjusted to the specific problems expected from the utilisation of the fuel (derived from the interpretation of fuel indexes) as well as the constraints of the process where it shall be applied in future. TGA, chemical fractionation, SEM/EDX analyses, TGA/DSC as well as TEC can be used as supporting tools to gain deeper insights into specific aspects, and to gain basic data (e.g. kinetic data) for process modelling.

If a new fuel has positively been evaluated by these methods with regard to an application in real-scale it is recommended to finally perform a pilot-scale test run with this fuel. Thereby, the plant settings can already be optimised based on the results gained from the advanced fuel characterisation.

# 1 Introduction and background

Biomass fuel characterisation is a relevant issue for all thermo-chemical conversion technologies. At present biomass fuel characterisation is mainly done by chemical or TGA analysis. Within the last years several national and international projects were initiated, which focus on advanced biomass fuel characterisation techniques in order to define the behaviour of a fuel during the pyrolysis, gasification and combustion stage as good as possible and thus support the proper design of a conversion plant.

Already performed and ongoing R&D work on advanced biomass fuel characterisation focuses on advanced analyses methods such as chemical fractionation, the definition of suitable fuel indices for biomass fuels and suitable models to describe the release behaviour from biomass fuels for an improved simulation of the subsequent gas phase conversion processes. Moreover, suitable models based on thermodynamic equilibrium calculations (TEC) to evaluate the ash melting behaviour are under investigation. In recent years also new advanced biomass fuel characterisation techniques based on lab-scale reactors have been developed respectively are under development which focus on the characterisation of the release behaviour of NO<sub>x</sub> precursors and ash forming elements (e.g. K, Na, Zn, Pb, S, Cl) during the different conversion stages. Moreover, they are also used for the determination of conversion kinetics. Different lab-reactor designs are applied whereas the types of reactors (fixed bed, fluidised bed, single particle reactors, etc), the operation conditions (pyrolyses/gasification/combustion mode) and the sample intake and the kind of operation (batchwise or continuous operation) are manifold. Consequently, also the data that can be gained from tests at these different reactors vary significantly depending on the heating rates, atmospheres and reactor type applied.

Advanced fuel characterisation is also of great relevance since “new” biomass fuels come up which are not yet well characterised (e.g. short rotation coppice, energy grasses, biomass residues from industry as well as residues from pyrolysis and liquid biofuel production like char and hydrolytic lignin). These fuels usually contain elevated amounts of ash forming elements (especially of K), S, Cl and N. Consequently during their thermal conversion often problems with ash melting, deposit formation, corrosion as well as gaseous S-, Cl- and N-compounds occur. Sometimes they additionally show decomposition characteristics which significantly differ from conventional biomass fuels. As a consequence, advanced fuel characterisation methods are needed to make quick evaluations regarding these risks possible for a certain biomass fuel. By that way, the need for the performance of cost intensive real-scale trials can be minimised.

## 2 Objectives of advanced fuel characterisation within the field of thermal biomass conversion with special respect to “new” biomass fuels

The advanced fuel characterisation methods presently used or under development have their advantages within a certain application range. Therefore, the current Task 32 project has been initiated in order to

- gain an overview about advanced biomass fuel characterisation techniques presently applied,
- discuss the strengths and weaknesses of the different methods as well as their specific fields of application, and
- assess the different methods with special respect to their applicability for the investigation of new biomass fuels.

For the latter aspect generally two approaches have to be considered, namely a *scientific* and an *industrial approach*. For scientific studies it is relevant to gain detailed basic information about new fuels and their behaviour in thermal conversion processes with the aim to

- gain a deeper understanding of the influences of their specific compositions on detailed mechanisms for e.g. pollution formation (e.g. NO<sub>x</sub>, SO<sub>x</sub>, HCl, particulate matter, etc.) or ash related issues (slagging, deposit formation, corrosion),
- gain basic data for the setup, the validation of models regarding fuel decomposition and ash and pollutant formation.

Fuel characterisation methods applied in this field have therefore to be accurate and repeatable, have to provide reliable data under well-defined framework conditions and are sometimes also tailored to demands for specific input data for a later modelling of certain processes.

In contrast, from an industrial perspective, simplicity, reproducibility, cost and time efficiency as well as the direct applicability of the results regarding expected problems in real-scale conversion systems are aspects of major relevance. In this respect, two cases have to be considered:

- Advanced fuel characterisation can be useful to decide if a new fuel is suitable for application in a certain existing conversion plant.
- Advanced fuel characterisation can be used during the initial design phase of a new conversion plant which shall be designed with special respect to a certain fuel spectrum to be applied.

### 3 Methodology

At first, BIOS in co-operation with IPPT/TU Graz worked out a questionnaire regarding advanced fuel characterisation methods (see ANNEX A) and distributed it via the Task members and some additionally selected R+D institutions. The questionnaire contains detailed questions regarding different advanced fuel characterisation methods and aimed to provide the basis for the evaluation of the current status concerning the development and application of advanced biomass fuel characterisation methods. Regarding the different methods it has been asked to describe them, to mention their advantages and disadvantages and to assess their applicability for advanced fuel characterisation. A special focus was thereby also on questions regarding the application of special lab-scale reactor concepts (varying from small-scale batch reactors to larger continuously working reactors).

In total, feedback from 22 institutions and laboratories has been received and evaluated. Two of the organisations are utilities, while the remaining 20 are research organisations or

university institutes. In this report the results of these assessments are always presented according to the following scheme: 5 grades leading from 1 (best assessment) to 5 (worst assessment).

Moreover, additional information was gained from already finalised and on-going international research projects which deal among other aspects also with advanced fuel characterisation methods:

- EU FP7 project *BRISK* (The European research infrastructure for thermochemical biomass conversion)
- ERA-NET Bioenergy project *FutureBioTec* (Future low emission biomass combustion systems)
- ERA-NET Bioenergy *SciToBiCom* (Scientific tools for fuel characterization for clean and efficient biomass combustion).

The data, information and experiences gained from these sources were finally supplemented by information gained from literature and summarised in the present report.

It has to be pointed out that since most of the leading research institutions active in the field of biomass fuel characterisation from the Task member countries have been incorporated in this evaluation, the most relevant methods for advanced fuel characterisation should be covered by this report. However, especially regarding purpose build lab-scale reactors a great variety of different devices can be found in both literature and responses to the questionnaires and therefore, this report does not claim to cover the complete range of existing devices but rather provides a representative overview of methods.

## **4 Discussion of different advanced fuel characterisation methods**

### **4.1 Chemical fuel analyses as a basic tool to apply advanced methods**

Although chemical fuel analysis is strictly not an advanced fuel characterisation method, it shall briefly be discussed at the beginning since it provides the state-of-the-art in fuel characterisation and the basis for many other methods discussed hereafter. It has to be pointed out that representative fuel sampling is a relevant prerequisite to gain reliable fuel analyses data. Therefore, sampling should be done according to EN 14778.

According to the survey performed, 64% of the institutions use chemical fuel analyses at their own laboratories. 77% of the institutions contract fuel analyses as a whole or regarding distinct parameters (which they cannot determine at their own labs) to specialised laboratories. A brief summary of the standards most commonly applied is provided in Table 1.

**Table 1:** Methods and standards commonly applied for biomass fuel analyses

Explanations: the table summarises the most commonly used methods according to feedback from the returned surveys

Parameter	Method	Title	Description
moisture content	EN 14774	Solid biofuels - Determination of moisture content - Oven dry method	The sample of biofuel is dried at a temperature of 105 °C in air atmosphere and the percentage moisture calculated from the loss in mass of the sample
ash content	EN 14775	Solid biofuels - Determination of ash content	The ash content is determined by calculation from the mass of the residue remaining after the sample has been heated in air under rigidly controlled conditions of time, sample weight and equipment specifications to a controlled temperature of (550±10) °C.
volatiles content	EN 15148	Solid biofuels. Determination of the content of volatile matter	Determination of the loss in mass, less that due to moisture, when a solid biofuel is heated out of contact with air under standardised conditions.
Fixed carbon	Usually calculated as 100% – moisture content - volatiles content – ash content		
C	EN 15104	Solid biofuels - Determination of total content of carbon, hydrogen and nitrogen - Instrumental methods	A known mass of the sample is burnt in oxygen, or in an oxygen /carrier gas mixture, under conditions such that it is converted into ash and gaseous products of combustion, which consist mainly of CO <sub>2</sub> , H <sub>2</sub> O, N <sub>2</sub> and/or oxides of nitrogen, oxides and oxyacids of sulfur and hydrogen halides. The products of combustion are treated to ensure that any hydrogen associated with sulfur or halides products of combustion is liberated as water vapour, oxides of nitrogen are reduced to elemental nitrogen, and those products of combustion which would interfere with the subsequent gas-analysis procedures are removed. The carbon dioxide, water vapour and nitrogen mass fractions of the gas stream are then determined quantitatively by appropriate instrumental gas analysis procedures
H	EN 15104		
N	EN 15104		
S	EN 15289	Solid biofuels - Determination of total content of sulfur and chlorine	Combustion in an oxygen bomb and absorption of the acidic gas components in an absorption solution. Determination of S and Cl by ion chromatography, ICP or other suitable analytical methods
Cl	EN 15289		
major ash forming elements	EN 15290	Solid biofuels - Determination of major elements - Al, Ca, Fe, Mg, P, K, Si, Na and Ti	The sample is digested in a closed vessel by the help of reagents, temperature and pressure. The digestion is either carried out directly on the fuel (part A) or on a 550 °C prepared ash (part B). The detection of the elements may be done by Inductively Coupled Plasma Optical Emission Spectrometry (ICP/OES), Inductively Coupled Plasma Mass Spectrometry (ICP/MS) or Flame Atomic Absorption Spectrometry (FAAS)
minor ash forming elements	EN 15297	Solid biofuels - Determination of minor elements - As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, V and Zn	The analysis sample is digested in a closed vessel made from a fluoro polymer using nitric acid, hydrogen peroxide and in some cases hydrofluoric acid in a microwave oven or a resistance oven or heating block. The digest is then diluted and the elements are determined with suitable instruments.
ash melting behaviour	CEN/TS 15370-1	Solid biofuels - Method for the determination of ash melting behaviour - Part 1: Characteristic temperatures method	A test piece made from the ash is heated and continuously observed. The temperatures at which characteristic changes of shape occur are recorded.

Regarding the determination of the ash content it must be mentioned that, as stated in EN 14775, differences in the ash content determined at a higher temperature (815 °C, according to ISO 1171-1997) compared to 550°C occur. They can be explained by the loss of volatile inorganic compounds, further oxidation (higher oxidation state) of inorganic compounds and the decomposition of carbonates forming CO<sub>2</sub>. In the ash content found in practise, for instance in a combustion plant, some of the released inorganic compounds are likely to be recovered in the fly ash while CO<sub>2</sub> and other gaseous compounds will mainly be released with the flue gas.

It has to be pointed out that besides the analyses methods and standards dedicated to biomass analyses (see Table 1) some labs also apply standards which have been developed for coal (ASTM D 3682 and ASTM D 3683 for instance for major and minor elements) or standards usually applied for soils or waste waters (e.g. DIN EN ISO 11885). Moreover, for major and minor element analyses sometimes also X-ray spectrometry on ashed fuel samples is applied.

It is strongly recommended to apply the methods listed in Table 1 since they have been developed and validated for biomass fuels (see e.g. [1]) and therefore provide the highest level of accuracy.

## **4.2 TGA analyses**

### **4.2.1 Description of the method**

Thermogravimetric analysis (TGA) allows a simultaneous determination of both mass loss and thermal history of a sample exposed to a heating program. This technique is generally used to study mass changes in relation to changes in temperature. This data can provide information concerning the partial degradation processes of a biomass sample. The ability of these systems to work with very small samples and until moderate heating rates are the keys to work under conditions assuring kinetic control.

The moisture content and the volatile and the char content of a biomass sample can directly be derived from TGA experiments. Moreover, when applying appropriate models, the reaction rate and the kinetic parameters for biomass decomposition can be evaluated. Furthermore, it is possible to determine the contents of the pseudocomponents hemicellulose, cellulose and lignin as well as reaction rates for their decomposition including kinetic data.

### **4.2.2 Commonly applied hardware**

A great variety of equipment for TGA from different manufacturers is available on the market. The principle of these devices is based on a small sample holder made of inert material (e.g. Al<sub>2</sub>O<sub>3</sub>, Pt) where the sample is placed. The sample holder is connected with a high precision microbalance and placed in an oven which enables a controlled heating of the sample according to a defined heating ramp/programme (most commonly constant heating rates are applied in order to facilitate the investigation of decomposition kinetics). During the experiment the oven is purged with a constant gas flow – depending on the test programme the utilisation of e.g. N<sub>2</sub>, He or Ar (inert atmosphere) or mixtures of N<sub>2</sub> and O<sub>2</sub> (oxidising atmospheres) is generally possible. Over the experiment temperature and mass loss (balance signal) are measured continuously.

Some manufacturers additionally offer a coupling of the TGA with analysers (mass spectrometers, FT-IR) which enable on-line analyses of the gases released from the sample during heating.

### 4.2.3 Typical operation parameters

In the following typical constraints of TG experiments are listed.

**Sample preparation:** The sample should be changed as little as possible by the sample preparation process. The sample should not be contaminated by the sample preparation process. The morphology of the sample influences the diffusion rate of reaction products and in turn the course of the reaction. At the same time, it also affects heat transfer within the sample. Therefore, it is important in quality control measurements to use a consistent and reproducible sample preparation technique.

**Sample pre-treatment:** Sample pre-treatment has a considerable effect on the pyrolytic behaviour of especially agricultural fuels or by-products. The high amount of inorganic salts in these species, especially potassium, has a very strong effect on pyrolysis. The typical shape of the DTG curve of biomass materials with a peak at high temperatures and a shoulder at lower ones can be totally altered by the inorganic salts present in agricultural products. Reducing the inorganics by washing the samples with cold distilled water removes a large amount of them and consequently, the differences between the pyrolytic behaviour of the biomasses are reduced. However, small differences between grassy and woody biomasses persist.

**Sample mass:** Usually in the range up to 200 mg depending on the device used and the sample holder volume. Most commonly a sample intake between 3 and 50 mg is applied.

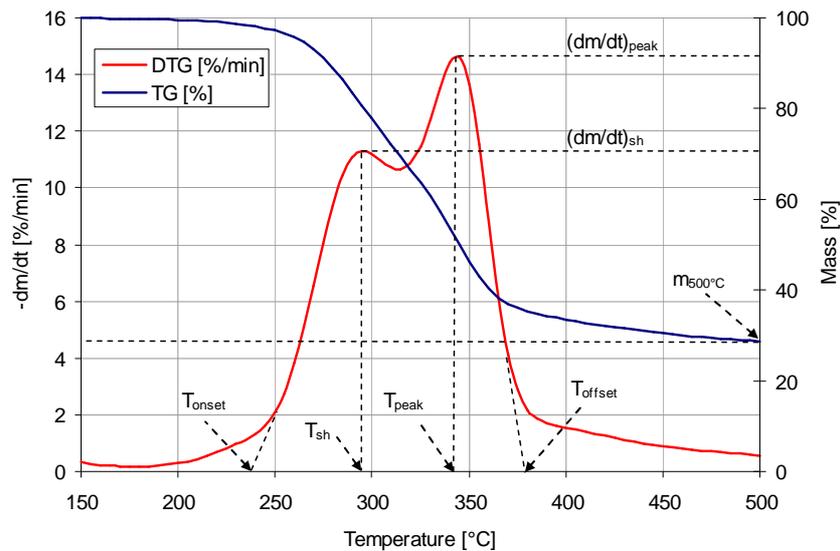
**Atmosphere (purge gas):** For pyrolyses tests: inert (N<sub>2</sub>, He, Ar)  
For combustion tests: various mixtures of N<sub>2</sub> and O<sub>2</sub>  
The purge gas flow is device dependent.

**Heating rate:** 5 to 100 °C/min; most commonly 5 to 50 °C/min  
It has to be considered that usually with increasing heating rate the char yield decreases [2].

### 4.2.4 Parameters evaluated

As a result of a TGA experiment the TGA plot shows the decomposition (mass loss) of the sample as a function of temperatures (see Figure 1). Moreover, the 1<sup>st</sup> derivative of the TGA curve, the so-called DTG curve provides the decomposition rate at a distinct temperature.

The thermal behaviour of the samples can be quantified through several parameters related to the temperature ranges of the different zones, devolatilisation rates and the char yields. Typical and widely applied parameters are introduced in Figure 1.



**Figure 1:** Definition of characteristics of thermogravimetric curves

Explanations: abbreviations: see text below; example of a test run under inert atmosphere

- $T_{onset(hemicellulose)}$  ( $T_{onset(hc)}$ ) represents the start of the hemicellulose decomposition determined by the extrapolation of the DTG curve.
- $(-dm/dt)_{sh}$  and  $T_{shoulder}$  ( $T_{sh}$ ) represent the overall maximum of the hemicellulose decomposition rate and the corresponding temperature, respectively.  $(-dm/dt)_{sh}$  and  $T_{sh}$  are typical characteristics of the hemicellulose decomposition.
- $(-dm/dt)_{peak}$  and  $T_{peak}$  represent the overall maximum of the mass loss rate and the corresponding temperature, respectively.  $(-dm/dt)_{peak}$  and  $T_{peak}$  are characteristics of the cellulose decomposition.
- $T_{offset}$  represents the end of the cellulose decomposition determined by the extrapolation of the DTG curves.
- $m_{500^{\circ}C}$  is the char yield at 500°C.

#### 4.2.5 Models applied for peak separation and the evaluation of thermal decomposition kinetics

Given the key role played by the devolatilisation stage in biomass conversion processes, numerous researchers have intensively investigated the kinetics of hemicellulose, cellulose and lignin decomposition as well as biomass pyrolysis. Generally it can be distinguished between so-called model-free and model-fitting methods. Within model-free methods the activation energy along the conversion process is calculated without a definition of a reaction model. These models do not distinguish between hemicellulose, cellulose and lignin decomposition. Typical examples are methods according to Friedman, Kissinger–Akahira–Sun, Ozawa–Flynn–Wall and Vyazovkin.

Model-fitting methods on the other side pre-define a certain reaction order model (e.g. 1<sup>st</sup> order model) and then calculate the kinetic parameters (activation energy, pre-exponential factor, etc.) with a fitting routine. This can be done by using a one step reaction approach (single reaction step model) or by assuming several competitive parallel reactions (model of pseudocomponents) [3, 4, 5].

## **4.2.6 Assessment regarding the applicability for advanced biomass fuel characterisation including a summary of strengths, weaknesses and opportunities**

15 of the 22 institutions (68%), who gave feedback within the survey, indicated that they frequently apply TGA analyses for biomass fuel characterisation.

During recent years TGA has become a standard tool in the investigation of the thermal decomposition of biomass fuels. The method is widely applicable. Another strength of the method is that it is rather quick and shows a very good reproducibility provided that the experimental constraints (sample preparation, atmosphere, mass applied, temperature ramp, etc.) are kept constant.

Especially the latter aspect also includes one weakness of the method when comparing results from different laboratories. Since different devices are applied and since there is no common standard regarding parameters such as sample pre-treatment, sample mass, heating ramp, etc., the results may vary. It has for instance been shown that

- the fuel pre-treatment may influence the results [6]
- different heating rates may lead to different char yields [2]
- the sample mass may also have an effect on the results [7]

Consequently, inter-laboratory comparisons have to be handled with care.

Due to the low sample mass applied within TGA analyses sample preparation and especially sample homogenisation play an important role. Multiple determinations are therefore strongly recommended.

Moreover, it has to be mentioned that kinetic parameters derived from TG experiments are related to the heating rate at which the experiment has been performed and that usually pulverised fuel is utilised to ensure that a pure kinetic regime prevails. Therefore, a direct application of these kinetic parameters to processes at which other constraints regarding heating rate and particle size prevail should be done with caution since there may be transport limitations and the kinetics may also not be valid at very different heating rates.

## **4.3 Fuel indexes**

### **4.3.1 General concept**

Fuel indices are calculated from biomass fuel analyses data. Thereby, the physical behaviour, chemical reaction pathways and the interactions between different elements respectively groups of elements during combustion are taken into account. The application of fuel indexes has a long lasting history starting with indexes for coal combustion more than hundred years ago. After the beginning of burning high-sulphur coals rich in pyrites ( $\text{FeS}_2$ ) on grates, it was quickly recognised that pyrite was responsible for the formation of clinkers. For the first time a combustion related problem was directly related to a specific mineral species. It was understood that iron occurring in high sulphur coals acted as fluxing agent, lowering the melting temperature of quartz and clays found in coal. These early problems associated with slagging were the trigger for the development of empirical correlations for the prediction of

slagging tendencies. The correlations describe the relationship between the melting temperature of slag and the proportional distribution between basic and acid constituents [8].

After the increasing electricity demand since the 1950s as well as the ambition to increase the electric efficiency resulted in continuously increasing steam temperatures. Also the use of more problematic coals resulted in further fireside problems like ash sintering or slagging, fouling of convective heat recovery surfaces and high temperature corrosion. Therefore, various empirical correlations especially to predict the ash sintering behaviour of coal have been developed [8].

It was seen that indexes developed for coal cannot be applied for biomass [9]. Since coal is a type of sedimentary rock, minerals can occur disposed as tiny inclusions within minerals, layers, nodules, fissures and rock fragments. Thick layers and abundant nodules are removed by standard preparation facilities. The thinner layers and nodules stay in the coal and typically consist of aluminium silicates (clay, illite, kaolinite, feldspar) and silicon oxide (quartz). The alkali metals (typically Na) are bound in this aluminium silicate structure and occur in minor overall concentrations. In biomass fuels in contrast K exists in high concentrations and its chemical binding in the organic fuel matrix is different to coal. Si as a further example is introduced in the plants by absorption of silicate acid from the soil. Si is deposited as a hydrated oxide usually in an amorphous form, but occasionally in crystalline form. Depending on the biomass species the major elements responsible for the ash chemistry can roughly be categorised in low Si/ high Ca containing fuels e.g. wood and woody biomass and high Si/ low Ca containing fuels e.g. herbaceous biomass. It can generally be said that coals contain higher amounts of S mostly in the form of  $\text{FeS}_2$ . In biomass plants S exists as sulphates or organic sulphur. The amount of Cl in coal depends on the coal type and exists predominantly as inorganic alkali chlorides and a smaller amount of unspecific organic chlorides. In biomass Cl appears as a chloride ion, where its concentration is closely related to the nutrient composition of the soil. The difference in occurrence and in chemical binding of certain elements explains the non-applicability of empirical coal correlations for sintering or slagging, fouling and high temperature corrosion on biomass fuels.

Far less empirical correlations or fuel indexes predicting combustion related problems have so far been found for biomass [e.g.: 10, 11, 12]. A comprehensive summary of fuel indexes for biomass combustion, their application and interpretation is provided in [9].

### **4.3.2 Fuel indexes applied and their interpretation**

In the following, different fuel indexes presently applied for biomass fuels are summarised. Generally, these fuel indexes can be divided into two main categories which are related to

- Formation of emissions of gaseous pollutants
- Ash related problems (slagging, fouling, fine particulate emissions, corrosion)

#### **4.3.2.1 Fuel indexes related to the formation of gaseous pollutants**

##### ***N content as an indicator for the NO<sub>x</sub> emission potential***

In biomass combustion processes NO<sub>x</sub> emissions (emissions of NO and NO<sub>2</sub> calculated as NO<sub>2</sub>) mainly result from fuel-N while their formation from combustion air (prompt and thermal NO<sub>x</sub> formation) plays only a minor role [13, 14, 15]. It has been shown that although

with increasing N-content of the fuel the release of NO<sub>x</sub> precursors to the gas phase decreases, the net NO<sub>x</sub> emissions increase. Based on available data gained from real-scale fixed-bed combustion systems according to their N-contents biomass fuels can be categorised as follows:

- low N fuels (< 0.4 wt.% d.b.) – e.g.: wood fuels
- medium N fuels (0.4 - 1 wt.% d.b.) – e.g.: short rotation coppices (SRC), kernels and straw
- high N fuels (1 - 10 wt.% d.b.) – e.g.: cereals and waste wood.

Experience shows that many new biomass fuels are medium or high N fuels (e.g.: SRC, cereals, energy grass), thus NO<sub>x</sub> emissions >200 mg/Nm<sup>3</sup> (related to dry flue gas and 13 vol% O<sub>2</sub>) have to be expected. Thus the application of primary and secondary measures for NO<sub>x</sub> emission reduction may play an important role when utilising these fuels.

#### ***Molar (K+Na) / [x\*(2S+Cl)] ratio as an indicator for HCl and SO<sub>x</sub> emissions***

It has been shown that during combustion processes S and Cl show an almost constant release ratio from the fuel to the gas phase of 80 to 90% respectively > 90% [8]. During combustion S and Cl preferably form alkaline (K and Na) sulphates and chlorides. Cl and S, which are not bound by these elements to the solid phase, form gaseous emissions, namely HCl and SO<sub>x</sub>. To describe the embedding of S and Cl in K and Na compounds, the fuel index (K+Na) / (2S+Cl) (molar ratio) has been developed [10]. In fluidised bed systems it has been observed that alkaline surplus leads to availability of alkaline metals with the bed material and therefore, high values of the index (K+Na) / (2S+Cl) lead to increased risks for bed agglomeration [10].

In order to fine-tune this evaluation, in [8] the factor “x” has been introduced which considers experimentally determined release rates for S, Cl, K and Na for different biomass fuels. Following, by this factor x only the S, Cl, K and Na released to the gas phase is considered which offers a much more adequate basis for an evaluation of HCl and SO<sub>x</sub> emissions to be expected. It has for instance been shown that for fixed-bed combustion systems HCl and SO<sub>x</sub> emissions are usually in a negligible range if the molar (K+Na) / [x\*(2S+Cl)] ratio is above 0.5 respectively 0.4. However, it has to be considered that S also forms Ca and Mg sulphates and to a smaller extent Ca and Mg chlorides can be formed. Since these interactions are not considered within the index, its evaluation can only be used as a rough indication whether problems regarding increased gaseous emissions have to be expected or not [9].

#### **4.3.2.2 Fuel indexes related to ash related problems**

##### ***The sum of K, Na, Zn and Pb (mg/kg dry fuel) as an indicator regarding aerosol emissions (fine particles smaller 1 µm) and the deposit formation potential***

This indicator can be used to evaluate if highly efficient dust precipitators (electrostatic precipitators - ESP, baghouse filter) will be needed to keep the particulate matter (PM) emission limits for a plant utilising a specific fuel. It is also an indicator for the deposit build-up on heat exchanger surfaces. This index is related to the formation of aerosols (particles with a diameter smaller 1 µm = PM<sub>1</sub>) during the combustion process and does not include coarse fly ashes.

Besides S and Cl, a part of the semi-volatile and volatile ash forming elements such as K, Na, Zn and Pb are released from the fuel to the gas phase during combustion. In the gas phase

these elements undergo homogenous gas phase reactions and later, due to supersaturation in the gas phase, these ash forming vapours start to nucleate or condense on the surfaces of existing particles or heat exchanger tubes.

Since in most biomass fuels K usually shows significantly higher concentrations than other aerosol forming elements (e.g. Na, Zn and Pb) the release of K is the most relevant parameter for this index. According to this index regarding aerosol emissions, biomass fuels may be categorised as follows [8].

- Low PM<sub>1</sub> emission range (up to about 20 mg/MJ): index < 1,000 mg/kg d.b.
- Medium PM<sub>1</sub> emission range (20 – 100 mg/MJ): index 1,000 - 10,000 mg/kg d.b.
- High PM<sub>1</sub> emission range (>100 mg/MJ): index > 10,000 mg/kg d.b.

### ***The molar Si/K ratio and Cl/Si ratio as an indicator for the K release***

A high molar Si/K ratio leads to a preferred formation of potassium silicates which are bound in the bottom ash [16, 17]. Therefore, the K release is reduced. For very high Si/K ratios, (i.e. >15 for sewage sludge) a good embedding of K in the bottom ash and consequently a very low K release prevails. However, for low Si/K ratios (< 2.5) no clear conclusion can be made concerning the dependency of the K release on the Si/K ratio [6]. In [19] the molar Cl/Si ratio is proposed to assess K release. Cl supports the release of K while Si reduces the release by embedding K in the bottom ash. Therefore, with increasing value of the index the K release increases. However, other parameters such as the fuel bed temperature, the association of K in the fuel as well as reactions with Ca and P seem to have a strong influence on the K release. Consequently, both indexes mainly work well in Si-K-dominated systems (e.g. straw and other Si-rich agricultural fuels).

### ***Indicators for ash melting problems***

Several fuel indexes can be applied to estimate the ash melting properties. It is generally well known that Ca and Mg increase, whereas Si in combination with K decreases the ash melting temperature [12, 18, 20]. The molar Si / (Ca+Mg) ratio can therefore provide first information about ash melting tendencies in ash systems dominated by Si, Ca, Mg and K [12]. However, for P-rich systems, this correlation is not valid. In combination with Si a modified index (Si+P+K) / (Ca+Mg) can be introduced. With this index also for P rich fuels a prediction regarding the ash melting behaviour is possible.

Generally fuels with high ash melting temperatures (when considering the shrinkage starting temperature as a measure) such as wood fuels show values of both indexes in the range of <1 while herbaceous fuels such as straw, which typically show very low ash melting temperatures (<1,000°C), show values of >2.5 for the index Si/(Ca+Mg) respectively >5 for the index (Si+P+K) / (Ca+Mg).

### ***The molar 2S/Cl ratio as an indicator for high-temperature corrosion risks***

S and Cl show almost constant release ratios for different biomass fuels [6]. Both elements are relevant for aerosol and deposit formation since in the gas phase they form alkaline sulphates and alkaline chlorides which subsequently form particles or condense on heat exchanger surfaces. Therefore, a link between the 2S/Cl ratio in the fuel and in the aerosols respectively deposits formed prevails. For fuels with high 2S/Cl ratios a protective sulphate layer is formed

at the tube surfaces. According to [21] only minor corrosion risks have to be expected for 2S/Cl ratios in the fuel of  $>4$ . It is additionally suggested that the molar 2S/Cl ratio in the fuel should be at least 8 to achieve negligible chlorine levels in boiler deposits, and thereby to eliminate corrosion from this source.

#### **4.3.3 Assessment regarding the applicability for advanced biomass fuel characterisation including a summary of strengths, weaknesses and opportunities**

11 of the 22 institutions (50%), who gave feedback within the survey, indicated that they frequently apply fuel indexes analyses for biomass fuel characterisation. The satisfaction with and applicability of this method was assessed with the grade 2 by 30%, the grade 3 by 30% as well as the grade 4 and 5 by 20%.

Fuel indexes bear the advantage that they are quickly and easily calculated from results of chemical analyses. This simplicity can be mentioned as the major strength of this method which makes it suitable for a quick pre-evaluation of a fuel.

There are, however, also some weaknesses which have to be carefully considered when applying fuel indexes for fuel characterisation.

- The interpretation of fuel indexes is based on results from real-scale combustion. Therefore, it has to be taken care that the reference data are from combustion technologies comparable with the one under consideration (e.g.: NO<sub>x</sub> formation in fluidised bed combustion differs from fixed-bed combustion due to the different temperatures and stoichiometry conditions in the fuel bed).
- Fuel indexes have been evaluated for a certain range of biomass compositions. If a new biomass fuel significantly deviates from these ranges, an extrapolation may not be permitted, especially regarding the evaluation of ash related problems.

Generally, some fuel indexes such as the N-content as an indicator for NO<sub>x</sub> emissions, the 2S/Cl ratio regarding corrosion risks as well as the sum of K, Na, Zn and Pb regarding the aerosol formation potential can be assessed as reliable since they have shown an acceptable statistical performance for a broad range of biomass fuels investigated so far.

Also the ash melting indexes show an acceptable accuracy but they have to be handled with care since their evaluation is usually based on data gained from the standard ash melting test (CEN/TS 15370-1 – see Table 1). This test is based on the investigation of ashed fuel samples. The composition of these samples deviates from those of real-scale ashes since the fractionation of certain elements in the different ash fractions is not considered. During combustion relevant shares of S, Cl, K, Na as well as easily volatile heavy metals are released to the gas phase and therefore their concentrations in the bottom ash will be depleted and in the fly ash fraction higher than in the fuel ash sample used for the ash melting test. However, the ash melting indexes can provide reproducible trends as well as a good first estimate on the ash melting behaviour.

The indexes  $(K+Na) / [x \cdot (2S+Cl)]$  as well as Si/K may provide valuable first indications however, interactions with other ash forming elements as well as influences of other process parameters such as fuel bed temperature and atmosphere may lead to significant variations regarding the absolute values and therefore, they can only indicate rough trends. Especially for

new biomass fuels the application of the index  $(K+Na) / [x \cdot (2S+Cl)]$  is only useful if experimental data for the definition of the factor  $x$  are available.

With an increased utilisation of fuel indexes for different fuel assortments and an increased understanding of the underlying mechanisms a further improvement of fuel indexes as a tool for advanced fuel characterisation can be expected within the coming years. Supported by this trend, fuel indexes might be further developed from a purely qualitative to a semi-quantitative method for biomass fuel characterisation in future.

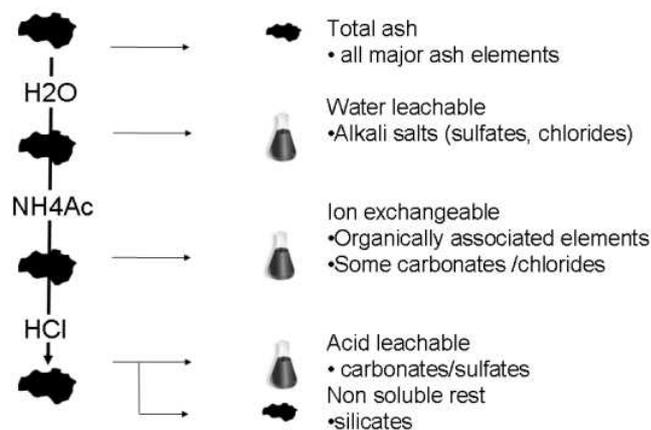
## 4.4 Chemical fractionation

### 4.4.1 Theoretical background

Chemical fractionation is a method based on selective leaching by water, ammonium acetate and hydrochloric acid. The method was originally developed by Benson and Holm [22] for the characterization of coal. Baxter [23] used a modified version for the characterization of 7 biomass fuels. At Åbo Akademi University, Finland, the method has been further developed for biomass and waste characterisation. This method can be helpful when determining how ash-forming elements are bound in the fuel [24, 25].

### 4.4.2 Description of the method

Figure 2 presents a simplified scheme showing that the stepwise leaching distinguishes between different types of ash-forming matter in a fuel according to their solubility in different solvents.



**Figure 2:** Simplified scheme of the fractionation procedure [26]

Fuel samples are milled to a particle size below 5 mm to facilitate handling and acceptable leaching times. Too small particles have shown to clog filters, whereas too large particles demand a too long leaching time. Increasingly aggressive solvents, i.e. water (H<sub>2</sub>O), 1M ammonium acetate (NH<sub>4</sub>Ac) and 1M hydrochloric acid (HCl) leach samples into a series of four fractions (including the unleached residue) for analysis. The amounts of leaching agents as suggested by [22] and [23] cannot be applied when leaching dry biomass fuels. It is difficult to achieve proper mixing for most fuels. Instead, an excess of water (up to 500ml/50g fuel for agricultural residues) should be used in the first step, firstly to achieve proper wetting of the samples, secondly to achieve proper leaching [24, 25]. These problems are not

encountered in the other leaching steps, since the solid samples here are already thoroughly wet from the previous steps and extensive washing.

The increasingly aggressive solvents leach samples into a series of four fractions (including the unleached residue). The untreated samples, the liquid fractions and the remaining solids are analysed.

### **4.4.3 Interpretation of results**

Typical main ash-forming components, which are leached out by water include alkali sulfates, -carbonates, -phosphates and -chlorides. Elements leached out by  $\text{NH}_4\text{Ac}$  are believed to be organically associated, such as Mg, Ca as well as K and Na. HCl leaches the carbonates and -sulfates of alkaline earth and other metals. Silicates and other minerals remain mainly in the insoluble residue. Heavy metals are usually leached out at low pH, with an exception of Zn, Pb and Mn that also may be present in water soluble and/or ion exchangeable forms [26].

### **4.4.4 Assessment regarding the applicability for advanced biomass fuel characterisation including a summary of strengths, weaknesses and opportunities**

6 of the 22 institutions (27%), who gave feedback within the survey, indicated that they at least sometimes apply fuel chemical fractionation for biomass fuel characterisation. The satisfaction with and applicability of this method was assessed with the grade 2 by 50% and the grade 3 by 50%.

Chemical fractionation is an interesting tool to investigate the way how ash forming elements are bound in a biomass fuel. It can provide a much more detailed image of fuel associations than e.g. a bulk chemical analysis and gives a preliminary idea on the reactivity of inorganic elements.

However, the data have to be evaluated and interpreted with care since especially regarding the water soluble part of K, S and Cl comparisons with lab-scale reactor tests often show an overestimation of the reactivity leading to too high release predictions. Moreover, the direct practical interpretation of the results is rather problematic since high temperature interactions as they occur during the real combustion process are not considered with this method. A further criticism regarding this fuel characterisation method was that it is rather time consuming and expensive.

## **4.5 SEM/EDX analyses**

### **4.5.1 Fields of application**

SEM (Scanning electron microscopy) and EDX (energy dispersive x-ray spectrometry) are generally seen as common tools in fuel analyses. Especially in coal combustion CCSEM (computer-controlled SEM) is frequently applied to determine the size, composition, abundance, and association of mineral grains in prepared coal samples. Moreover, they are also applied to investigate ash and deposit samples.

Regarding biomass combustion this technique is more often used for ash, slag and deposit analyses as well as corrosion studies but is rather unusual for fuel characterisation. If it is

applied for fuel characterisation, either ashed fuel samples are analysed regarding their contents of major ash forming elements or fuel samples are ashed at different temperatures in order to investigate ash transformation. The latter investigations are usually performed in the course of scientific studies.

#### **4.5.2 Description of the method**

##### *Pulverised fuel analyses (CCSEM analyses)*

Pulverised fuel is fixed in a mounting medium, contrastive to organic and mineral matter. The sample is scanned by means of automated frame-by-frame SEM/EDX analyses. An image/particle recognition software is applied to identify particles and records the diameter and the elemental composition (typically some 1,000 particles per sample are scanned). A mineral classification algorithm translates the elemental compositions (the associations of elements) into mineral compounds which are likely to be present. The results are expressed as minerals (w/w %) as a function of particle size. More detailed information can be taken from [27].

##### *SEM/EDX analyses of ashed fuel samples*

The fuel is ashed at a defined temperature in oxidising atmosphere and then the ash is sealed in resin. The resin block is cut and the cutting area is dry polished. The polished surface is then steamed with e.g. carbon to make it conductive. Several analysis options are possible with scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX). The most commonly applied are:

- Optical assessment of shape and structure of the individual mineral phases using SEM.
- Element analyses of defined areas (area scans) and points (spot scans) of the surface using EDX.
- Element mapping which provides a qualitative distribution of element concentrations over a defined area.

In general, the same analyses methodology is also applied for ash, slag and deposit samples originating from real-scale plants.

#### **4.5.3 Interpretation of results**

SEM/EDX analyses allow for a morphologic and chemical evaluation of single ash particles and therefore can provide a deeper insight into ash chemistry. For the interpretation of results of course experienced personnel is needed.

#### **4.5.4 Assessment regarding the applicability for advanced biomass fuel characterisation including a summary of strengths, weaknesses and opportunities**

Compared with bulk analyses SEM/EDX analyses of ashed fuels provide the advantage that single ash particles can be investigated. This on the other side has the disadvantage that due to the arbitrary selection of single particles it is not secured that the average overall ash composition is adequately represented. Moreover, the detection limits for trace elements are

much higher and the accuracy of the method is much lower compared to chemical analyses. Therefore, the application of SEM/EDX for fuel analyses can only be recommended for the investigation of specific phenomena as well as ash transformation processes (analyses of samples ashed at different temperatures).

Regarding the characterisation of ashes, slags and deposits as well as for corrosion studies the outstanding value of SEM/EDX analyses is indisputable since they provide the possibility to investigate single particles as well as different phases in a rather quick and accurate way. However, in the course of advanced fuel characterisation these kinds of analyses can only be applied as a supporting tool for e.g. lab-scale reactor tests and not as a stand-alone tool.

8 of the 22 (36%) institutions, who gave feedback within the survey, indicated that they apply SEM/EDX whereas the clear main focus is on the investigation of ashes, slags and deposits and not on the direct evaluation of biomass fuels. The satisfaction with and applicability of this method was assessed with the grade 1 by 25%, the grade 2 by 50% and the grade 3 by 25%.

## **4.6 Thermodynamic high temperature equilibrium calculations**

### **4.6.1 Theoretical background**

Thermodynamic high temperature equilibrium calculations (TEC) are a commonly used tool for predicting the chemical behavior of complex systems. It is often based on the minimization of the Gibbs energy of the system, which can be calculated using modern software if thermodynamic data exist for the phases considered. Thermodynamic data for multi-component solution phases are based on the thermodynamic data of the end-member components and on the interaction parameters of the solution model describing the Gibbs energy of the solution phase. The computational methods involved in calculating multi-phase and multi-component thermodynamic chemical equilibria revolve around Gibbs energy minimization.

For advanced fuel characterisation TEC are mainly applied to estimate the ash melting behaviour, the release of inorganic species from the fuel to the gas phase as well as for corrosion studies.

### **4.6.2 Commonly applied software codes and databases**

The most common software code applied for TEC is FACTSAGE but also other codes such as HSC or in-house developed codes are used. Even more relevant than the software code are the thermodynamic databases applied. Therefore, before starting a calculation, it has to be checked if reliable thermodynamic data are available for the system to be investigated. It is for instance well known that for P-phases as well as for certain mixtures of Al and Si a lack of reliable data exists. This can especially be of importance regarding agricultural fuels where P often plays a relevant role in the ash chemistry. In any case thermodynamic databases as well as the selection of the components considered within the calculations have to be treated with care.

### 4.6.3 Interpretation of results

The elemental composition of the fuel or an ash as well as of the gas phase (i.e. combustion or gasification agent) forms the input dataset for TEC. As a result TEC provide the composition of gaseous, liquid and solid phases at defined temperatures respectively over defined temperature ranges. Therefore, it is possible to for instance evaluate the amount and composition of molten phases, phase transformations as well as the release of inorganic elements and compounds from the solid to the gas phase. The quality of the results however strongly depends on the quality of the thermodynamic data used and the correct definition of the system boundaries. It has additionally to be considered that TEC always provides results for thermodynamic equilibrium which may not be reached in real-scale applications. Moreover, kinetic limitations (e.g. the reaction of  $\text{SO}_2$  to  $\text{SO}_3$  during biomass combustion processes) are not considered. These restrictions are one reason why for a correct performance of the calculations as well as for the detailed evaluation of the results experienced personnel with advanced knowledge in ash formation and ash chemistry is needed. Otherwise, a considerable risk for misinterpretations exists.

### 4.6.4 Assessment regarding the applicability for advanced biomass fuel characterisation including a summary of strengths, weaknesses and opportunities

8 of the 22 institutions (36%), who gave feedback within the survey, indicated that they apply TEC for advanced fuel characterisations. The main fields of application can thereby be assigned to ash melting studies (7 positive replies), release studies (8 positive replies) as well as corrosion studies (3 positive replies). The assessment for TEC regarding these investigations scatters between grade 2 and grade 4.

As advantages of TEC it can be mentioned that

- they are rather cheap, quick and the software codes are in principle easy to use
- they can provide detailed insights into ash chemistry and ash transformation processes
- they allow for the simulation of the behaviour of different ash fractions

These advantages make TEC a suitable method to derive trends and qualitative and sometimes semi-quantitative assessments. On the other hand there are restrictions and limitations given which do normally not allow for a quantitative prediction based on TEC which are:

- TEC do not consider kinetics and it is thus not secured that equilibrium is reached for a certain system investigated.
- The models applied must consider the stoichiometry in the fuel bed accurately. The release of Zn for instance strongly depends on the presence of reducing or oxidising atmosphere.
- Especially for P-phases the thermodynamic data presently available are doubtful.

Concluding, if carefully applied, TEC can be a valuable and helpful tool in advanced biomass fuel characterisation. They can provide a deeper insight and a better understanding of the chemical reactions of relevance but they are not suitable for quantitative interpretations.

## 4.7 TGA/DSC analyses

### 4.7.1 Principle

With DSC (differential scanning calorimetry) the difference in the amount of heat required to increase the temperature of a sample and a reference is measured as a function of temperature. The sample and reference are maintained at nearly the same temperature during the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned.

### 4.7.2 Fields of application

For biomass fuel samples the heat of reaction can be determined. Regarding the characterisation of biomass ash samples mainly the investigation of phase changes by the identification of endothermic and exothermic peaks is of interest (e.g.: carbonisation processes, release processes, melting processes).

### 4.7.3 Commonly applied hardware including typical operation parameters

Usually simultaneous TGA / DSC analyses equipment, so-called STA (simultaneous thermal analyses) is applied. Various manufacturers offer appropriate equipment on the market. Typical operation parameters are:

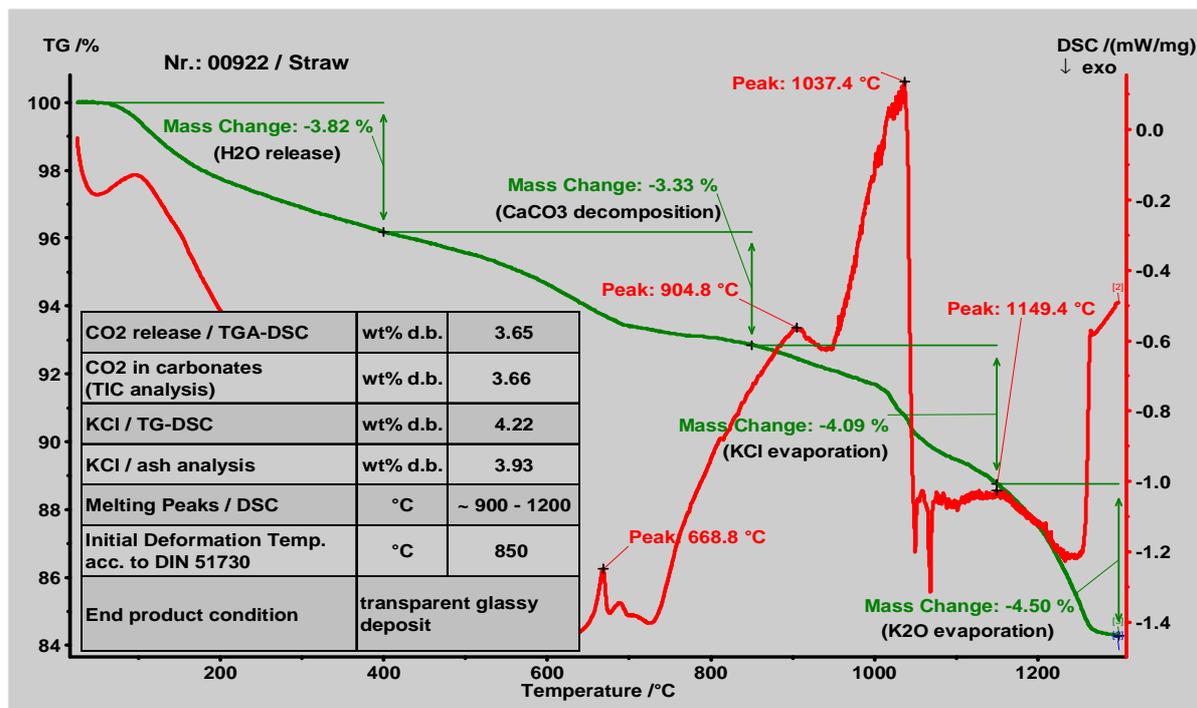
Sample preparation:	The samples must be grinded
Sample mass:	usually in the range up to 30 mg
Atmosphere:	inert (N <sub>2</sub> ) or air
Heating rate:	10 to 20 °C/min
Temperature range:	up to 1,500°C (depending on the kind of equipment)

### 4.7.4 Interpretation of results

For analyses of ashes either ash samples from real-scale plants or ashed fuel samples can be used. In Figure 3 a typical result for a TGA/DSC run with an ashed straw sample (ashed at 550°C) is presented [26]. Straw has a typical ash composition with silicon and potassium as the dominating elements and contains smaller amounts of chlorine and sulfur. The mass changes (green line) up to 400°C are generally assumed to be evaporation processes of physically and chemically bound H<sub>2</sub>O (crystal water). The STA curve shows further in the temperature range of 400 to 850°C a mass loss of 3.33 wt% w.b. characterized by an endothermic peak at 669°C, which is caused by CaCO<sub>3</sub> decomposition and release of CO<sub>2</sub> (in Figure 3 for comparison also results of TIC-analyses of the initial sample are mentioned which are in a good agreement with this finding). The mass decrease observed in the temperature segment from 850 to 1,150°C may primarily be attributed to KCl evaporation which is in good agreement with existing literature data as well as with results of wet chemical K and Cl analyses of the initial sample as well as the residues after the test run (see table in Figure 3). In this temperature segment simultaneously the initial melting of the ash sample occurs. The endothermic peaks at 905°C and 1,037°C, along with the peak at 1,149°C,

can be assigned to different stages of ash melting. The mass loss above 1,150°C may be explained by  $K_2O$  release most probably caused by the decomposition of slags consisting of K and Si.

As the example above shows, the interpretation of results from TGA/DSC tests demands for experienced personnel since knowledge about ash transformation, ash melting and release processes is needed.



**Figure 3:** Results of simultaneous thermal analysis (STA) for straw ash [26]

Explanations: TG (thermogravimetric analysis)... mass loss in % w.b.; DSC...differential scanning calorimetry; sample mass: 20.51 mg; heating rate: 10 K/min; atmosphere: synthetic air

#### 4.7.5 Assessment regarding the applicability for advanced biomass fuel characterisation including a summary of strengths, weaknesses and opportunities

7 of the 22 institutions (32%), who gave feedback within the survey, indicated that they apply DSC for advanced fuel characterisations. The assessment of the applicability of DSC scatters between grade 1 and grade 3.

DSC respectively STA measurements bear the advantage that they can be performed with small samples of ashes or ashed fuels, that they are rather quick, show a good repeatability and can provide scientifically relevant data regarding phase changes as well as ash melting behaviour.

Relevant weaknesses and restriction to be mentioned are related to the sample pre-treatment. If milled ash samples from real-scale plants are applied it has to be considered that the grinding process may have an influence on the results. If ashed fuel samples are applied it has to be taken into account that these ashes have not been formed during a real combustion process with its different stages and that they represent with the exception of Cl and S (which

are partly released during ashing) the composition of the fuel ash. Therefore, their compositions may deviate from ashes produced in real-scale plants under considerably higher temperatures (where also release of volatile and semivolatile species such as alkaline metals and heavy metals takes place).

DSC analyses are mainly performed in the course of scientific work as a supporting tool for e.g. thermodynamic equilibrium calculations regarding the behaviour of ash forming elements.

## 4.8 Special purpose built batch reactors

### 4.8.1 Main fields of application

The fuel characterisation techniques introduced in the previous sections either provide qualitative data (fuel indexes, chemical fractionation, TEC) or provide quantitative data related to distinct conditions (TGA related to heating rates, STA regarding ash melting and ash transformations) and can therefore not be applied for the quantitative evaluation of relevant fuel characteristics under real-scale process conditions. In order to also gain these data, different types of lab-scale batch reactors have been developed. The aim of the application of such reactors is to gain relevant information regarding certain fuel characteristics under well-controlled lab-scale conditions which may be adjusted in a way that they also allow comparisons with real-scale processes.

Various parameters can be investigated in such reactors. The feedback from the survey conducted comprised in total 10 different reactors applied by different institutions. In Table 2 a brief summary of the parameters investigated in these reactors is presented.

**Table 2:** Parameters investigated in different batch reactors

Parameter	% of positive replies
decomposition behaviour	100%
decomposition kinetics	100%
char formation	80%
mass loss during conversion	90%
fuel temperature (particle or fuel bed) during conversion	70%
composition of the flue gases	100%
release of NO <sub>x</sub> precursors	40%
release of inorganic elements	60%
ash melting behaviour	40%

### 4.8.2 Description of the setup including measurements and analyses coupled with the reactors

All reactor types described in the following are in-house developments of different research groups and therefore no market available serial products. Different reactor concepts are principally applied which are:

- Heated grid reactors

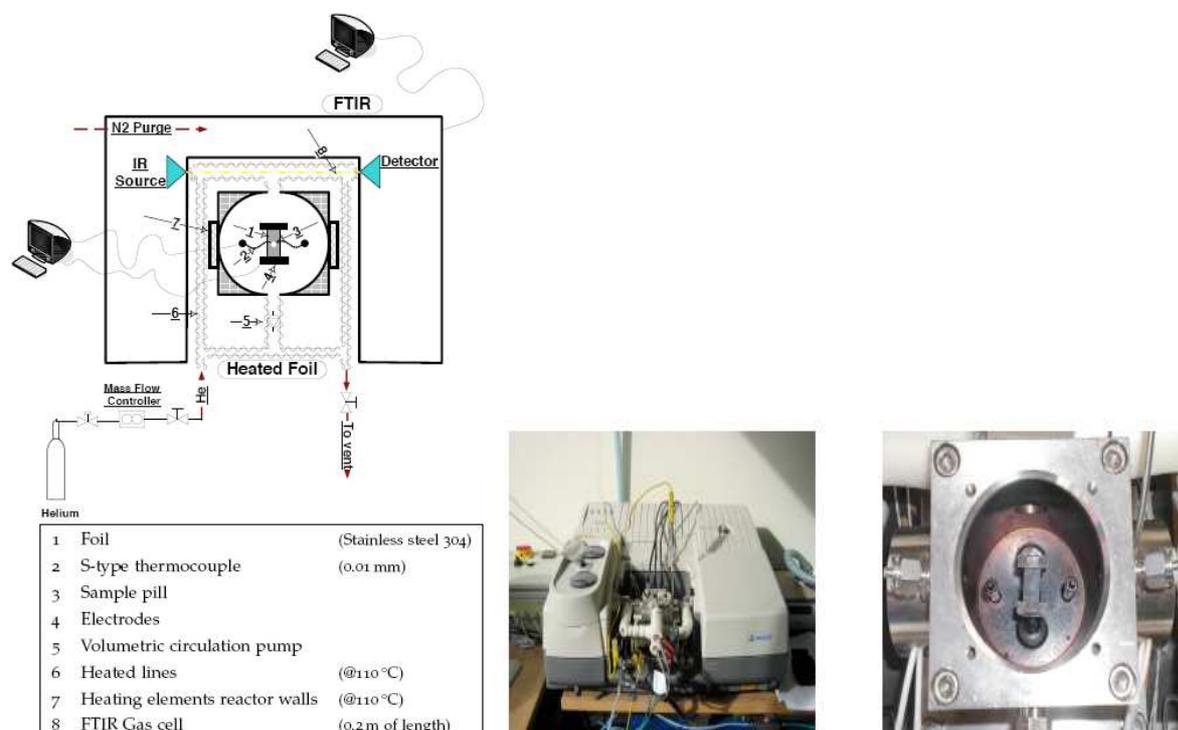
- Single particle reactors
- Fixed-bed reactors

Regarding the field of application 9 of the 10 reactor concepts covered by the survey mainly focus on the investigation of the thermal decomposition behaviour of biomass fuels as well as the release of NO<sub>x</sub> precursors and inorganic elements to the gas phase. In these reactors a fuel sample is heated to a specified temperature and different parameters such as the mass loss as well as the release of certain compounds are measured either by on-line analyses of the gases produced or by chemical analyses of the initial fuel sample and the remaining residues (charcoal or ashes). In contrast to these reactors the so-called slag analyser is a purpose build reactor solely developed for the investigation of the slagging behaviour of biomass pellets. In the following typical reactor setups are briefly introduced.

### *Heated grid reactor*

Heated grid reactors (also sometimes called wire-mesh reactors) are applied to carry out experiments regarding biomass devolatilization and char gasification at high heating rates (up to 1,000 K/s) under a chemically controlled regime. Small amounts of sample (~10 mg) are placed between two wire-meshes (grids) or foils and heated by pulse intervals of electric current. Usually, solid, liquid and gaseous products from the reactor are then subjected to various analyses (e.g. online FT-IR analyses or off-line input and output material analyses). The setup can also be used for tests with in-situ diagnosis technologies such as Raman-holography and high-speed imaging.

In Figure 4 a scheme as well as images of a heated grid reactor with an in-situ FT-IR-coupling applied at TU Delft is shown as an example [28, 29, 30, 31].



**Figure 4:** Heated grid reactor at TU Delft

### ***Fixed bed and single particle reactors***

Within the survey performed 8 reactors of this type have been identified. Even though different setups are applied the main characteristics of these reactors are well comparable. In the following the most relevant construction parts as well as operation parameters/conditions are listed.

Retort:	The core of these reactors is a cylindrical retort in which the fuel sample is placed. Manifold materials such as steel, SiC ceramics as well as quartz glass are applied for this retort. The diameters of the retorts are typically between 30 and 150 mm and the lengths vary between 350 and 1,400 mm.
Heating strategy:	All reactors are electrically heated.
Operation temperatures:	Depending on the construction material and the power of the indirect heating system maximum operation temperatures of 900 to 1,200 °C can be achieved.
Heating rates:	Up to some 100 K/min are possible but the heating rate applied strongly depends on the design of the individual test run.
Atmosphere:	A broad field of different reaction media such as air, N <sub>2</sub> , steam or different gas mixtures is applied depending on the setup of the respective test run. Therefore, inert, reducing and oxidising conditions can be adjusted.
Sample mass:	The sample intake varies from about 10 mg to some 100 g.
On-line measurements	6 of the 8 reactors are equipped with balances for on-line mass-loss determinations. 7 of the 8 reactors are coupled with flue gas analysers. O <sub>2</sub> and CO measurements are common whereas some reactors are also coupled to NO, SO <sub>2</sub> as well as multi-component FT-IR analysers or micro GC. A rather unique direct coupling of a single particle reactor with an ICP-MS is presently operated at BIOENERGY2020+ in Graz (AT). This setup provides the unique possibility to gain on-line data regarding the release of K, Na, Zn, Pb, S and Cl during fuel decomposition.

In Figure 5 pictures of some typical reactor setups are presented. In the following, as examples, these reactors are also briefly described.



**Figure 5:** Pictures of different batch reactors for biomass fuel characterisation

Explanations: top from left to right: Fixed bed reactor at the CHEC Research Centre, Technical University of Denmark (DTU) (DK) [32, 33], Single-particle reactor at the Department of Chemical Engineering, Åbo Akademi (FIN) [34, 35, 36], bottom from left to right: Fixed-bed lab-reactor at Institute for Process and Particle Engineering, Graz University of Technology (AT) [37]; Single particle reactor at BIOENERGY2020+, Graz (AT)

#### *Fixed bed reactor at the CHEC Research Centre, Technical University of Denmark*

The reactor consists of a two-zone electrically heated oven (max. Temperature: 1,200°C), in which a cylindrical alumina tube ( $\text{Ø}60$  mm; lengths: 1400 mm) is mounted horizontally, having water-cooled flanges at both ends. A sample (e.g. biomass) can be inserted in the middle of the reactor. The reactor can then be sealed and a gas (mixture) can be introduced into the reactor, for example to pyrolyse or combust the sample. The sample temperature and the exit gas composition (e.g.,  $\text{O}_2$ ,  $\text{CO}$ , and  $\text{CO}_2$ ) can be monitored online, so that the conversion process can be followed during an experiment. After the desired residence time,

the sample holder can be withdrawn from the reactor, weighed, and finally the residue can be collected for chemical analysis.

The setup allows for conversion (pyrolysis and combustion) of solid fuel samples under well-controlled conditions (temperature, gas flow rate and composition, and residence time), simulating the conditions on the grate of a real-scale boiler. By performing accurate weight measurements and chemical analysis of the sample before and after the treatment in the reactor, quantitative data can be obtained on the release to the gas phase of inorganic elements from relatively small samples. Such data are important for the understanding and modeling of ash and aerosol formation in grate-fired boilers.

#### *Single-particle reactor at the Department of Chemical Engineering, Åbo Akademi*

The reactor allows to study the thermal decomposition and combustion behaviour of biomass samples under various atmospheres as well as temperature ranges. It consists of a quartz tube inserted in an electrically heated ceramic furnace where the temperature can be varied from ambient temperature to 1,150°C. Premixed gases are supplied from the bottom and the middle of the reactor. Additionally a purging gas is supplied at the place of sample insertion. The flow of the gases is controlled by mass flow controllers. Different mixtures of CO<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> can be used as an oxidizing gas and nitrogen as a purging gas. The average residence time for the gases is around 20 s, while, considering only the product gases from devolatilization/combustion of the fuel, the residence time at high temperature is estimated at about 4 s. The temperature in the reactor is measured with a thermocouple inserted in the ceramic wall of the furnace, close to the surface of the quartz reactor in the proximity of the sample placement point. An insertion probe allows the sample (about 10 to 15 mg) to be placed on the sample holder in a room temperature environment and then to be inserted, in a fraction of seconds, into the hot reactor. The product gases can be analysed with analysers for CO<sub>2</sub>, CO, O<sub>2</sub>, NO and SO<sub>2</sub>. Moreover, an optical observation of the sample via an optical board and a camera is possible.

#### *Single particle reactor at BIOENERGY2020+*

The reactor consists of an electrically heated vertical ceramic main tube (height 755 mm, inner diameter 50 mm) connected with 4 horizontal side tubes (length 177 mm, inner diameter 28 mm) which is placed in a furnace. The sample (about 1 g) is placed on a grid which is mounted on a horizontal sample holder which is directly connected to a scale. The sample holder is inserted into the pre-heated furnace (temperatures from ambient temperatures up to 1,100°C can be achieved). At the sample two thermocouples are placed to measure the temperatures in the centre and at the surface of the particle. The carrier gas (various mixtures of air and N<sub>2</sub>) flows through the reactor from below and is heated until it reaches the position of the sample holder. During an experiment the mass loss as well as the centre and the surface temperature of the fuel particle are measured on-line. Moreover, after dilution with N<sub>2</sub> or Ar the gases released from the sample are on-line monitored by gas analysers as well as regarding K, Na, S, Cl, Zn and Pb by using an ICP-MS. By evaluating these measurements time-resolved information about the thermal decomposition process as well as regarding the release of main gas species and inorganic elements can be gained.

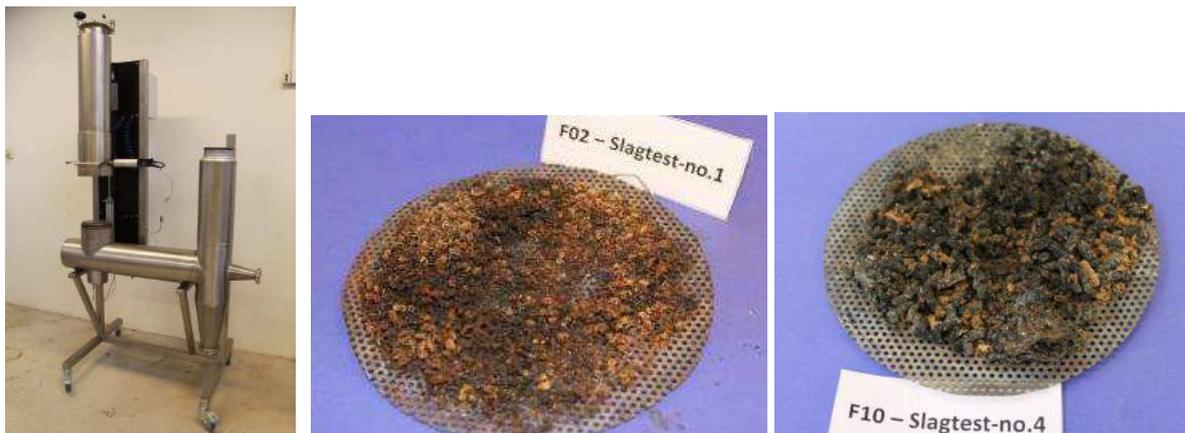
### *Fixed-bed lab-reactor at the Institute for Process and Particle Engineering, Graz University of Technology*

This lab-scale reactor has been designed to investigate the thermal decomposition and combustion behaviour of biomass fuels in packed beds. It consists of a cylindrical electrically heated retort made of silicon carbide. The fuel (100 to 400 g depending on the fuel density) is put in a cylindrical sample holder which is placed on a balance and inserted into the pre-heated reactor. Pre-heating is usually set to 450°C in the lower part (which surrounds the sample holder) and 750°C in the upper part (above the sample holder). Combustion air respectively inert gas (different mixtures of O<sub>2</sub> and N<sub>2</sub>) is then injected through the fuel bed. During fuel decomposition the sample mass loss as well as the temperatures in and above the fuel bed are recorded on-line. Moreover, downstream the reactor the composition of the flue gases produced is measured by various analysers (FTIR, Paramagnetism, NDIR, heat conductivity, FID, CLD) regarding its contents on O<sub>2</sub>, CO, CO<sub>2</sub>, NO, NO<sub>2</sub>, H<sub>2</sub>O, HCN, NH<sub>3</sub>, HCl, SO<sub>2</sub>, as well as a number of hydrocarbons.

The sample is placed in the sample holder, inserted into the pre-heated reactor and then a combustion air flow of typically 30 l/min (at 20°C) is initiated which is kept constant during the whole test run. By continuously measuring the mass decrease of the fuel, the temperatures at different positions in the fuel bed and the concentrations of the main flue gas species as well as of N-species, comprehensive information about the thermal decomposition process as well as the release of NO<sub>x</sub> precursors can be gained. Moreover, by analysing the fuel as well as the residual ash, information regarding the release of ash forming elements can be achieved. Test runs with this reactor also provide first indications regarding the slagging behaviour of a fuel (by visual observation).

### *Slag-analyser of the Danish Technological Institute*

The slag analyser (see Figure 6) has been developed at the Danish Technological Institute (DTI) in order to assess the slagging behaviour of biomass pellets.



**Figure 6:** Slag analyser of the Danish Technological Institute

Explanations: left: image of the slag analyser; middle and right: residues (slag and ash particles) after test runs; more information can be taken from [38].

It is a small-scale downdraft batch combustion unit. At the beginning of each test the fuel storage tank is filled with about 3 kg biomass pellets (depending on the ash content). The fuel rests on a pre-weighted grate made of a 1.5 mm stainless steel plate. For ash rich fuels some

pellets of a very low ash containing fuel are added in order to dilute the sample to prevent clogging of the grate. After closing the storage tank the fuel is ignited by hot air ventilation and the downdraft combustion takes place. During the test the temperature just below the grate is continuously recorded. After the fuel has been burnt and the system has cooled down all ash and slag residues are carefully collected from the walls and the grate for further assessment. The assessment includes the mass fraction of slag particles larger than 1.6 mm, the mass of slag sticking to the grate after the test run and the average size of the three largest slag lumps. For each parameter different thresholds are defined for final categorization of the fuel into one of five categories where category 1 represents the lowest and category 5 the highest potential for slagging.

### **4.8.3 Description of the test run protocol**

#### *Heated grid reactor*

At heated grid reactors the fuel sample is placed in the cold reactor. Then, the purge gas flow is initiated and finally a defined heating programme (adjusted to the objectives of the test run) is started. The test run duration is typically in the range of some seconds due to the low sample mass (some mg) and the high heating rates. Depending on the setup, the mass loss as well as the composition of the gases released from the sample can be analysed. Usually, chemical analyses of the initial sample material and the residues are also performed to calculate element balances over the test run.

#### *Fixed bed and single particle reactors*

Regarding the fixed bed and single particle reactor concepts the test protocol is rather flexible and is always adjusted to the objectives of the specific test. This concerns the heating ramps and final reactor temperatures, the gas atmospheres applied, the gas flows, the test run duration as well as the measurement and analyses programme applied. Typical test run procedures and protocols are described in [33 - 37].

At the fixed-bed reactor at the CHEC Research Centre, Technical University of Denmark, the fuel can be inserted into the cold reactor, then purge gas flow (with a composition adjusted to the atmosphere that shall be achieved) is initiated and finally a heating program (different heating ramps according to the objectives of the test run) as well as the accompanying on-line analyses of the gases at reactor outlet are started.

At the other reactors, within a first step the reactor is usually pre-heated to a target temperature. Then gas flow is initiated whereas the composition of the reaction medium (different mixtures of O<sub>2</sub>/N<sub>2</sub> or O<sub>2</sub>/N<sub>2</sub>/CO<sub>2</sub>) varies depending on the kind of experiment to be conducted (pyrolyses or combustion tests), the sample is introduced into the pre-heated reactor and the measurements are started. It is worth to mention that at the single particle reactors at Åbo Akademi and at BIOENERGY2020+ it is additionally possible to interrupt the process at a defined time by removing the sample and stopping the reactions with purge gas (N<sub>2</sub>). By this measure also different phases of the decomposition process can be investigated.

The duration of the single experiments depends on the sample mass as well as the heating programme applied and typically is in a range up to 1 hour.

At all reactors described the initial sample as well as the residues, which are removed from the reactor after the end of the test runs, are usually forwarded to chemical analyses as a basis for the calculation of element balances over the test run.

### *Slag analyser*

For the slag-analyser the testing protocol is rather fixed, as it can be seen from the description of this device.

#### **4.8.4 Restrictions**

The lab-scale reactors described bear the advantage that only a small sample mass is needed and that the conversion conditions can be well controlled and appropriately adjusted. However, the small samples applied also bear some restrictions regarding the shape and size of the biomass particles to be investigated. In a heated grid reactor for instance only very small particles can be investigated. Moreover, limited sample mass also results in rather small amounts of gases released from the samples which in some cases causes problems regarding gas analyses.

#### **4.8.5 Interpretation of results**

The interpretation of the results gained from batch reactors is always strongly related to the reactor set-up as well as the operating conditions. A single particle reactor for instance can provide no direct results about the behaviour of a fuel bed and on the other hand fuel and ash interactions in a fixed-bed reactor influence the results in a way that they are not directly applicable for the evaluation of the conversion of a single fuel particle. Moreover, heating rates and atmospheres can significantly influence the results gained. Therefore, the evaluation of the results is always strongly related to the test run setup and consequently is also only directly applicable for processes with comparable constraints.

#### **4.8.6 Assessment regarding the applicability for advanced biomass fuel characterisation including a summary of strengths, weaknesses and opportunities**

10 of the 22 institutions (45%), who gave feedback within the survey, indicated that they apply purpose built batch reactors for advanced fuel characterisations. The assessment of the applicability of the reactors scatters between grade 1 and grade 2 which underlines the high value of this kind of reactors for fuel characterisation.

The strengths of special purpose built batch reactors are:

- Rather small sample mass needed.
- Rather small time demand per experiment.
- Very good suitability for kinetic studies under well controlled and realistic constraints (for heated grids and single particle reactors).
- Possibility to gain comprehensive data and information regarding biomass decomposition and release of relevant compounds (NO<sub>x</sub> precursors, fine particulate forming elements).

## Weaknesses

- The systems are purpose built and usually not commercially available. Therefore, comparisons of results gained from different reactors must be handled with care due to the different constraints (e.g. sample mass, gas composition, heating rates, etc.).
- In all cases well educated and experienced personnel is needed to operate the reactors.

Due to the possibility to adjust the settings and conversion conditions in batch reactors in a very controlled way, the data gained can typically be translated to real-scale processes. Moreover, they can provide valuable basic information for model development and validation. This can concern models to describe the biomass conversion process itself (e.g. fuel decomposition as well as char oxidation models) but also models to simulate NO<sub>x</sub>, particulate matter and deposit formation.

## 4.9 Special purpose built continuously working reactors

### 4.9.1 Main fields of application

Within the survey performed 12 of 22 institutions (55%) declared to use continuously working reactors for fuel characterisation. With the exception of one reactor they are in-house developments. According to the feedback in these devices the following types of test runs and parameter investigations are performed.

**Table 3:** Test runs performed and parameters investigated in different continuously working reactors

	% of positive replies
<b>Type of experiments</b>	
devolatilization tests	75%
pyrolysis tests	58%
gasification tests	58%
combustion tests	83%
<b>Parameters investigated</b>	
decomposition behaviour	58%
kinetics	50%
char formation	58%
composition of the gases produced	83%
release of NO <sub>x</sub> precursors	50%
release of inorganic elements	58%
deposit formation	58%
gaseous emissions	83%
particulate emissions	75%

## 4.9.2 Description of the setup including measurements and analyses coupled with the reactor

Most common are entrained flow reactors (so-called drop tubes). Usually at these systems the fuel is injected on the top of a vertical reactor however, at BIOENERGY2020+ in Graz (AT) a design is applied where a fixed-bed combustor (grate fired combustion chamber) is coupled with a drop tube. Moreover, according to the feedback from the survey fluidised bed reactors (for the investigation of bed agglomeration) and a fixed bed gasifier (for dedicated gasification trials) are applied. Since drop tubes and entrained flow respectively tube reactors represent the most common continuously operated reactors for fuel characterisation and additionally offer a broad range of different operation modes and investigations to be performed, they are firstly discussed in the following in more detail.

### *Drop tube and entrained flow reactors*

Within the survey performed 6 reactors of this type have been identified. In the following the most relevant construction parts as well as operation parameters/conditions are listed.

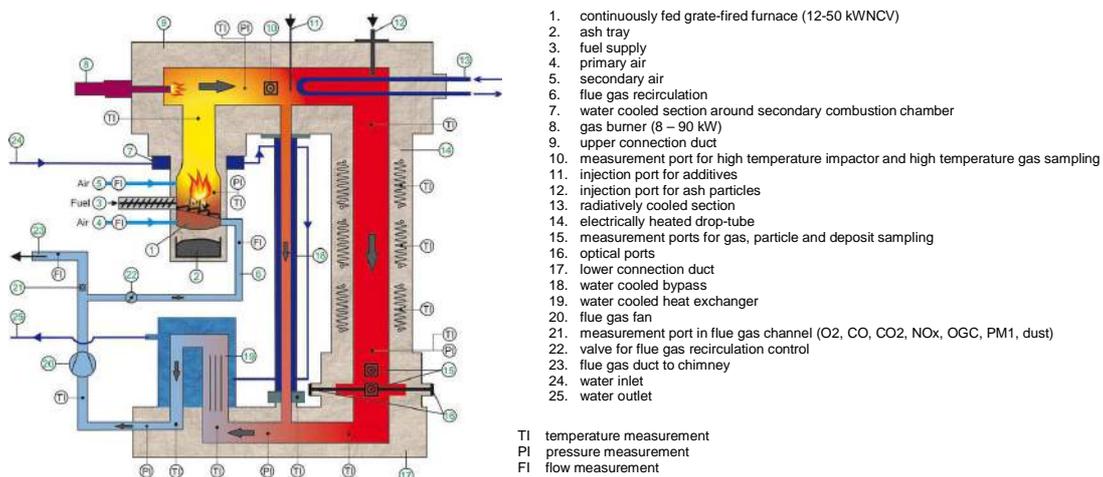
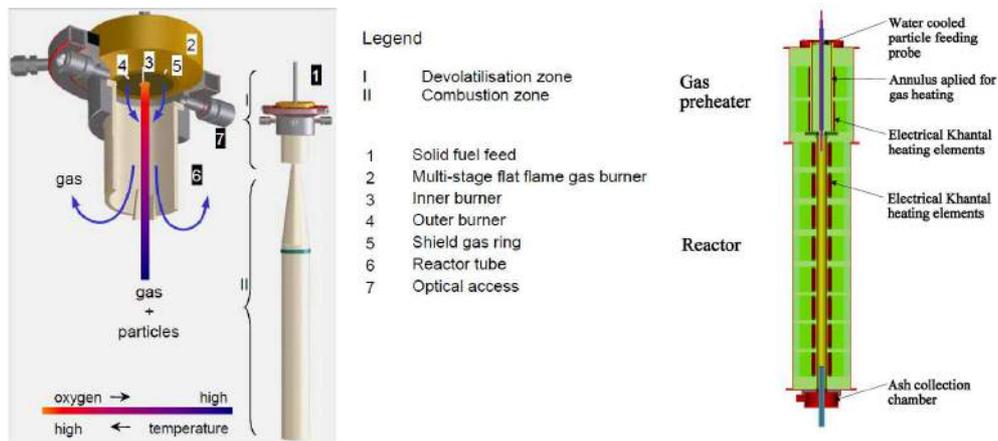
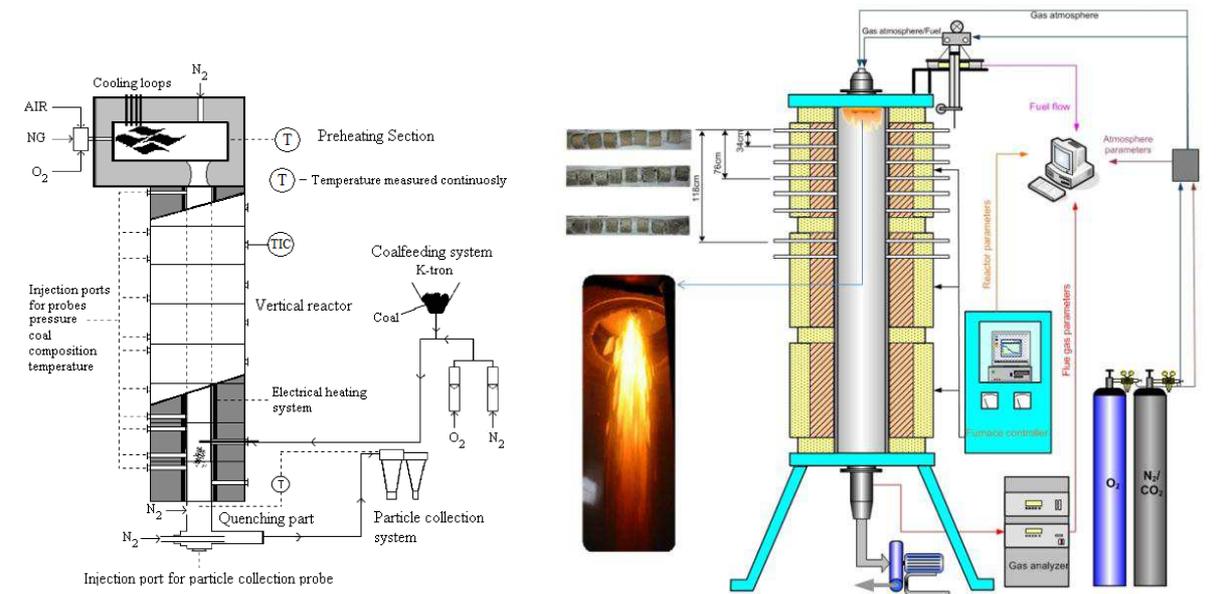
Drop tube:	The core of these reactors is a cylindrical tube which is usually made of ceramics ( $\text{Al}_2\text{O}_3$ or SiC). The diameters of these tubes are typically between 50 and 150 mm and the lengths vary between 1,300 and 4,000 mm.
Heating strategy:	All reactors are electrically heated and usually there is also a direct heating by combustion of the test run fuel or by a supporting gas burner flame.
Biomass combustion:	The fuel is in many cases injected and burned in a pre-mixed gas flame. One reactor is coupled to a grate-fired biomass furnace where the biomass is burned on a moving grate. Alternatively, this reactor can also be operated with a gas flame.
Operation temperatures:	Depending on the construction material and the power of the indirect heating system maximum operation temperatures of 800 to 2,250 °C can be reached. The most common range is between 800 and 1,600°C.
Operation pressure:	All reactors are operated at atmospheric pressure.
Biomass size:	With the exception of the drop tube connected to a grate-fired biomass furnace, which can utilise chipped and pelletised fuels all other reactors can only be operated with pulverised fuels (due to the underlying entrained flow concepts).
Biomass fuel flow:	Typical sample flows for entrained flow systems are 1 to 2 kg/h. The drop tube connected with a fixed-bed furnace can apply up to 20 kg/h
Atmosphere:	With the exception of the drop tube connected to a grate-fired biomass furnace which can only be operated with air, the other drop tubes can be operated with different gas mixtures as well as air.

**On-line measurements:** All reactors are coupled with flue gas analysers. O<sub>2</sub> and CO measurements are common. However, in principle all kinds of flue gas and product gas analysers can be applied depending on the objectives of the specific test run.

Additionally, at BIOENERGY2020+ in Graz an on-line corrosion probe is applied for corrosion studies with this reactor.

**Other measurements:** 4 of the 6 reactors apply different particle measurement techniques (e.g. low pressure impactors) as well as deposit probes in order to investigate slagging, deposit formation and corrosion related problems. These devices are usually inserted at drop tube outlet and also at varying heights of the drop tube (corresponds to different residence times of the flue gases in the reactor) if appropriate sampling ports are foreseen.

In Figure 7 pictures of some typical reactor setups are presented.



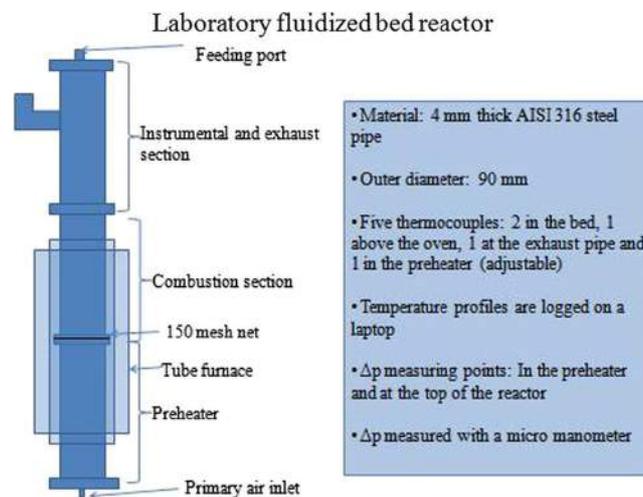
**Figure 7:** Pictures respectively schemes of different continuously working drop tube reactors for biomass characterisation

Explanations: top from left to right: IFRF IPFR (Isothermal Plug Flow Reactor) (IT) [39, 40], Wrocław University of Technology – plug-flow reactor (PL) [41, 42]; middle from left to right: ECN LCS (Lab-scale Combustion Simulator) (NL) [43, 44, 45, 46]; CHEC Research Centre, Technical University of Denmark (DK) entrained flow reactor [50, 51, 52, 53, 54, 55, 56, 57]; bottom: BIOENERGY 2020+ fixed bed furnace coupled with a drop tube (AT) [47, 48, 49]

### ***Fluidised bed reactor***

In order to investigate bed agglomeration related issues a laboratory-scale fluidised bed reactor has been designed and constructed at the Department of Chemical Engineering, Åbo Akademi. The reactor (see Figure 8) consists of a pre-heater (400 mm), a combustion section (500 mm) and the instrumental and exhaust section (520 mm). The reactor was designed so that it can be modified easily for different kinds of experiments. It was constructed using a 4 mm thick AISI 316 steel pipe with an outer diameter of 90 mm and an inner diameter of 82 mm. The reactor is electrically heated with a tube furnace to achieve a stable temperature and combustion conditions.

Temperature profiles and pressure drop over the bed are measured. A decrease in the pressure drop and an increase of the temperature difference between the upper and lower bed are used as indicators of agglomeration and defluidization. The reactor is equipped with a screw feeder that can feed fuel into the reactor at a constant rate.



**Figure 8:** Scheme of the lab-scale fluidised bed reactor at Åbo Akademi (FI) [58]

### ***Fixed bed gasifier***

At ENEA (IT) a fully equipped gasification plant (“PRAGA” – see Figure 9) based on a 200 kW<sub>th</sub> updraft gasifier is operated to test the gasification behaviour of different biomass fuels. The nominal input of the gasifier is 30-40 kg/h. The plant is operated slightly above atmospheric conditions and it uses a mixture of air and steam as gasification medium introduced under a moving grate at the bottom of the gasifier.

The produced gas moves upward from the bottom of the gasifier while the biomass particles move downwards progressively through zones of drying, pyrolysis, reduction and combustion. The gas cleaning section is composed by a biodiesel scrubber and two coalescer filters in series. By organic scrubbing, most of the organic and inorganic compounds (tars, HCl, etc.) are removed from the gas, while in the coalescer filters the oil drag particles are removed. This unit also allows a temperature reduction of the syngas coming out from the gasifier (about 300-400 °C). After the cleaning the gas is destined to a flare or to the hydrogen enrichment section HENRI.

The facility is equipped with several sampling probes/lines for solid, liquid (tar) and gas sampling. Moreover, it is extensively automated and remotely controlled with in-field flow-

meters, pressure and temperature measurements along the gasifier and the clean-up line for on-line monitoring.



**Figure 9:** Picture of the PRAGA plant [59]

### 4.9.3 Description of the test run protocol

As it can be seen from the description of the purpose built continuously working reactors a variety of different systems exists. Due to the characteristics of the reactors also a wide range of different experiments can be performed. Consequently, the test run methodology as well as the test run protocols change with respect to the objectives of the specific test runs. This concerns the framework conditions regarding gas atmospheres, reactor temperatures, flow conditions, residence times as well as the measurement setup. Typical test run procedures and protocols are described in [39-59].

### 4.9.4 Restrictions

Some of the reactor concepts discussed (mainly the drop tubes) provide the possibility to conduct test runs under a broad range of conditions regarding gas atmosphere (gasification as well as combustion trials) as well as temperature and to investigate a number of different parameters (see also Table 3). Other reactors on the other hand are purpose built for specific test runs such as the fluidised bed system at Åbo Akademi for the investigation of bed agglomeration and the PRAGA plant of ENEA for dedicated counter-current gasification tests.

One relevant restriction regarding all entrained flow reactors is the fact that due to the suspension firing only pulverised fuels can be applied and therefore a direct application of the data gained is only possible for suspension fired systems and not for fluidised bed or grate fired plants. If complete char burnout shall be achieved the maximum particle size is also limited due to the limited residence time available in the drop tubes.

The fixed bed reactor coupled with a drop tube at BIOENERGY2020+ in Graz (AT) is the only drop tube which utilises pellets and wood chips in a fixed-bed combustor. Therefore, data gained from test runs at this reactor are representative for grate combustion systems. However, gasification or pyrolysis trials can not be performed in this device since it is especially designed for biomass combustion, corrosion and deposit formation studies.

#### **4.9.5 Assessment regarding the applicability for advanced biomass fuel characterisation including a summary of strengths, weaknesses and opportunities**

Continuously operated reactors generally show a huge potential for advanced fuel characterisation. The main advantages are:

- Conditions in industrial processes can be reliably reproduced and therefore, the data are directly applicable to real-scale processes.
- Due to the continuous operation also long-term experiments including full mass balances as well as investigations regarding deposit formation and corrosion as well as bed agglomeration (for which typically extended test run durations are needed) are possible.
- Various analysers can be coupled to the reactors and therefore, a considerable number of different parameters can be measured and evaluated.
- Most of the drop tube reactor setups show a high flexibility regarding their application for pyrolysis, gasification and combustion tests.
- In some of the drop tube reactors sampling at different residence times of the fuel in the drop tube is possible and consequently the time dependent conversion process of a certain fuel can be studied in detail.

One relevant weakness of these reactors compared with the other methods mentioned in this report of course is that the equipment needed is complex and more cost intensive. Moreover, the operation costs of the reactors are also considerable since not only electricity and in many cases natural gas but also experienced personnel are needed to run the systems.

## **5 Comparison of the different methods**

The survey conducted has revealed that 73% of the institutions who gave feedback apply a certain strategy regarding biomass fuel characterisation. However, most of these institutions decide case by case and with respect to the final application (conversion process) as well as to the respective main topic of the investigation (decomposition behaviour, gasification/combustion behaviour, inorganic element release, etc.) which evaluation scheme they follow. Therefore, no clear trend regarding preferred advanced biomass characterisation tools could be derived from the survey.

Key parameters for the applicability of advanced fuel characterisation tools are

- time demand
- need for experienced and especially trained personnel
- market availability of the hardware and software needed to apply the method
- information depth gained
- applicability of the results with respect to real-scale process design respectively interpretation of results from an R&D and an industrial perspective

Based on the feedback gained from the survey a comparison of the different fuel characterisation methods discussed according to the key parameters mentioned is performed within Table 4 to Table 9.

**Table 4:** Application of the different methods by the participating institutions

Explanations: % of the participating institutions who apply the respective method

method	[%]
TGA analyses	38
Fuel indexes	50
Chemical fractionation	28
SEM/EDX analyses	36
TEC	36
TGA/DSC analyses	32
Batch reactors	45
Continuously working reactors	55

**Table 5:** Comparison of the different fuel characterisation methods discussed – time demand

method	time demand	comments
TGA analyses	low	rather low efforts for sample preparation; standardised, well automated procedures can be applied
Fuel indexes	low	can be calculated quickly based on chemical fuel analyses (if available)
Chemical fractionation	high	comprehensive not automated leaching procedure followed by chemical analyses
SEM/EDX analyses	low	rather low efforts for sample preparation; automated analyses procedures applicable
TEC	medium	the calculations run comparably quick and can be automated; a certain time effort is needed to check the databases as well as the models to be applied prior to calculations
TGA/DSC analyses	medium	rather low efforts for sample preparation; well automated procedures applicable; the critical evaluation of the results may be time consuming
Batch reactors	medium	preparation of the reactor setup and connection of all measurement devices and analysers may take time (depending on the complexity of the specific test setup); the experiments themselves are usually performed rather quickly (some minutes to about 1 hour per test run); analyses of the samples and the residues is also necessary
Continuously working reactors	high	preparation of the reactor setup and connection of all measurement devices and analysers as well as start-up usually is time demanding; due to the continuous operation and the sometimes "long-term" character of the experiments usually performed the testing campaigns may last for some hours up to some days; Usually comprehensive time consuming chemical analyses of feedstocks, residues as well as samples taken during the test run are needed

**Table 6:** Comparison of the different fuel characterisation methods discussed – need for experienced and especially trained personnel

method	need for experienced and especially trained personnel	comments
TGA analyses	low / medium	The operation of the equipment usually follows a clear procedure and can therefore be performed by laboratory personnel after a short training phase. The evaluation of the results (as long as standard evaluations are done) can be performed by personnel with a comparably low degree of experience in scientific work.
Fuel indexes	low / high	The calculation of the values can easily be done and also a first pre-evaluation can be done by medium experienced technicians based on guiding values available.
Chemical fractionation	low / high	The performance of the analyses follows a clear methodology and can be performed by laboratory personnel. For the evaluation of results experienced scientific personnel is needed.
SEM/EDX analyses	low / high	The performance of the analyses follows a clear methodology and can be performed by technical/lab staff. For the evaluation of results experienced scientific personnel is needed.
TEC	high	For the setup of the calculation model, the correct selection of elements and compounds to be considered, the selection of reliable databases and for the evaluation of the results highly experienced personnel is needed.
TGA/DSC analyses	low / medium	The operation of the equipment usually follows a clear procedure and can therefore be performed by laboratory personnel after a short training phase. The evaluation of the results (as long as standard evaluations are done) can be performed by personnel with a comparably low degree of experience in scientific work.
Batch reactors	medium	The realisation of a certain setup for the test runs can usually only be performed by experienced technical personal. For the performance as well as the evaluation usually medium experienced scientific staff it needed.
Continuously working reactors	medium / high	The realisation of a certain setup for the test runs can usually be performed by experienced technical personal. For the performance as well as the evaluation usually experienced scientific staff is needed.

**Table 7:** Comparison of the different fuel characterisation methods discussed – market availability of the hardware and software needed to apply the method

method	market availability of the hardware and software needed to apply the method	comments
TGA analyses	very good	A considerable number of different manufacturers and products exists (6 different suppliers within the 15 feedbacks received). Models for the evaluation of kinetic parameters are published in literature.
Fuel indexes	good	Calculation methods are available from literature
Chemical fractionation	very good	In principle chemical fractionation can be performed with the standard equipment available in analytical labs. Detailed methodological descriptions are available from literature.
SEM/EDX analyses	limited	Standard devices from different manufacturer are market available but expensive.
TEC	good / medium	Software codes (most commonly applied is FACTSAGE) are market available. The quality of the thermodynamic databases is sometimes insufficient and has to be checked. In some cases in-house data are applied which are not market available.
TGA/DSC analyses	very good	See TGA; methods regarding the evaluation and interpretation of the test runs can be taken from literature.
Batch reactors	low	Most of the lab-scale batch reactors applied are in-house developments. The single main parts (oven, balances, etc.) are in most cases standard equipment. However, especially the core of the reactor (retort) and the general setup are usually purpose built.
Continuously working reactors	low	These reactors have in most cases been developed within scientific projects and are therefore typically purpose built in-house developments.

**Table 8:** Comparison of the different fuel characterisation methods discussed – information depth gained

method	information depth gained	comments
TGA analyses	high	Can provide a full set of information regarding moisture, volatile and char content, contents of the pseudocomponents (hemicellulose, cellulose and lignin) as well as regarding decomposition kinetics in the respective gas atmosphere and heating regime.
Fuel indexes	low	Provide qualitative data for a quick pre-evaluation of combustion relevant parameters.
Chemical fractionation	medium	Can provide detailed information how inorganic elements are bound in a fuel but does not consider the influence of high-temperature interactions during thermal conversion.
SEM/EDX analyses	high	Information single ash particle basis can be gained.
TEC	medium	Information regarding the possible distribution of elements in different solid, molten and gaseous phases and compounds can be gained. The assumption of equilibrium and sometimes the limitation of databases available restrict the applicability of results.
TGA/DSC analyses	medium	Some restrictions regarding the correct interpretation of results, especially when complex ashes are investigated exist.
Batch reactors	high	Due to the high flexibility of most reactor setups regarding options for coupling with different analysers and measurement equipment as well as due to the possible adjustment of the operation conditions close to real-scale, very detailed information can be gained. It has however to be considered that in some cases limitations due to the low sample mass applied exist.
Continuously working reactors	very high	Due to the continuous operation and the usually good adjustment of the process to real-scale conditions.

**Table 9:** Comparison of the different fuel characterisation methods discussed – direct applicability to real-scale processes

Explanations: assessment based in 5 grades leading from 1 (best assessment) to 5 (worst assessment)

method	direct applicability to real-scale processes	comments
TGA analyses	2-3	2 regarding information on volatile and char contents 3 regarding the evaluation of reaction kinetics due to fuel pre-treatment (grinding) and heating rates applied which often deviate from real-scale applications
Fuel indexes	3	Qualitative data for a quick pre-evaluation
Chemical fractionation	3-4	Better applicable for scientific studies and in combination with other methods
SEM/EDX analyses	1-2	1 if ashes from real-scale plants are investigated and 2 for investigations of ashed fuel samples due to differences between a real-scale combustion and lab-ashing of fuels
TEC	3	Depending on the problem investigated and the quality of the thermodynamic databases available as well as the validity of the equilibrium assumption
TGA/DSC analyses	3-4	Better applicable for scientific studies and in combination with other methods
Batch reactors	1-2	Depending on the setup and the objective of the experiment
Continuously working reactors	1	Process constraints can be adjusted to real-scale processes

## 6 Combination of different methods in order to gain comprehensive information regarding a new biomass fuel

As it can be seen from Table 4 to Table 9, a considerable number of different methods with significantly differing applicability are available for biomass fuel characterisation. All these methods show their advantages and disadvantages and therefore, in many cases a combination of different methods is recommended. In the following some examples for such combinations are briefly discussed.

The evaluation of fuel indexes is a quick and rather cheap method for advanced fuel characterisation. Fuel indexes can provide a first pre-evaluation of relevant thermal conversion related properties of a biomass fuel and are therefore predestined as a first step in a comprehensive fuel evaluation procedure. Based on this method it is possible to identify potential problems with ash melting, corrosion as well as increased gaseous and particulate emissions. Therefore, fuel indexes are proposed to be applied always as a first step within advanced fuel characterisation in order to provide first indications which problems shall be further investigated with more detailed methods which may provide a higher information depth or a better direct applicability regarding conversion plant design and performance.

As a second step, test runs at lab-scale reactors are recommended in order to gain quantitative data regarding the parameters of interest under close to real-scale conditions. Batch reactor test runs can thereby be applied in order to investigate the fuel decomposition behaviour, the

release of aerosol forming elements, S, Cl and NO<sub>x</sub> precursors as well as the ash melting behaviour. Continuously working reactors can additionally provide information about deposit formation and corrosion related issues, the thermal conversion behaviour of a specific fuel as well as bed agglomeration in fluidised beds. The reactor type as well as the experimental setup (gas atmospheres and temperatures applied, measurements, sampling and analyses performed) have thereby to be selected according to the parameters which shall be investigated and the characteristics of a later real-scale conversion plant.

Chemical fractionation, STA, thermodynamic equilibrium calculations (TEC) as well as SEM/EDX analyses can additionally be applied as supporting tools in order to gain deeper insights in and a better understanding of ash transformation and ash melting processes as well as the release of inorganic species from the fuel to the gas phase regarding a specific fuel. Moreover, TGA tests can provide additional information on the hemicellulose, cellulose and lignin contents of a fuel as well as its decomposition kinetics. These data are especially of relevance for the modelling of biomass conversion processes.

The procedure presented provides comprehensive information regarding properties related to the thermal conversion of a specific new biomass fuel as well as regarding conversion related problems to be expected. If a new fuel has positively been evaluated by these methods with regard to an application in real-scale, it is recommended to finally perform a pilot-scale test run with this fuel. Thereby, the plant settings can already be optimised based on the results gained from the advanced fuel characterisation.

## 7 Summary and conclusions

A comprehensive questionnaire regarding advanced biomass fuel characterisation methods has been worked out and distributed to different organisations active in this field. In total feedback from 22 organisations has been received. Based on this feedback as well as on information and experiences gained from other European projects (EU FP7 and ERA-NET Bioenergy), a summary and evaluation of different advanced fuel characterisation methods has been made. The advanced methods concerned are TGA analyses, fuel indexes, chemical fractionation, SEM/EDX analyses, TGA/DSC analyses, thermodynamic equilibrium calculations as well as test runs at batch and continuously working reactors.

The evaluation of the questionnaires has revealed that obviously no commonly accepted strategy for advanced biomass fuel characterisation exists. Most labs apply a number of different methods and decide from case to case depending on the fuel and the targeted application which tools they are going to apply.

Summing up, the evaluation of the methods investigated shows significant differences in terms of time demand, need for experienced and especially trained personnel, market availability of the hardware and software needed to apply the method, information depth gained as well as applicability of the results with respect to real-scale process design.

It has been shown that generally, as expected, with increasing complexity of the method the information depth gained as well as the applicability of the data to real-scale processes increases. With this increase of information depth unfortunately also the costs and the time

demand for the tests as well as the need for experienced staff to perform the fuel characterisation as well as the evaluation work increases.

**TGA** has become a standard tool in the investigation of the thermal decomposition of biomass fuels. The method is widely applicable. A strength of the method is that it is rather quick and shows a very good reproducibility provided that the experimental constraints (sample preparation, atmosphere, mass applied, temperature ramp, etc.) are kept constant. However, no common standard regarding parameters such as sample pre-treatment, sample mass, heating ramp, etc. exist and therefore the results may vary if results from test runs under different conditions are compared. Moreover, kinetic parameters derived from TGA-experiments are related to the heating rate at which the experiment has been performed. Usually pulverised fuel is utilised to ensure that a pure kinetic regime prevails. Therefore, a direct application of these kinetic parameters to processes at which other constraints regarding heating rate and particle size prevail should be done with caution since there may be transport limitations and the kinetics may also not be valid at very different heating rates.

The **evaluation of fuel indexes** for the qualitative evaluation of combustion related aspects bears the advantage that it can be quickly and easily done based on results of chemical analyses. This simplicity can be mentioned as the major strength of this method which makes it suitable for a quick pre-evaluation of a fuel. But it has to be considered that the interpretation of fuel indexes is based on results from specific combustion tests. Therefore, it has to be taken care that the reference data are from combustion technologies comparable with the one under consideration. Moreover, fuel indexes have been evaluated for a certain range of biomass compositions. If a new biomass fuel significantly deviates from these ranges, an extrapolation may not be permitted, especially regarding the evaluation of ash related problems. Generally, some fuel indexes such as the N-content as an indicator for NO<sub>x</sub> emissions, the molar 2S/Cl ratio regarding corrosion risks as well as the sum of K, Na, Zn and Pb regarding the aerosol formation potential can be assessed as reliable since they have shown an acceptable statistical performance for a broad range of biomass fuels investigated so far. Other indexes such as the indexes related to ash melting like the molar Si/(Ca+Mg) ratio and the molar (Si+K+P)/(Ca+Mg) ratio, the molar index  $(K+Na) / [x \cdot (2S+Cl)]$  as an indicator for HCl and SO<sub>x</sub> emission potentials as well as the molar indexes Si/K and Cl/Si as indicators for the K release may provide valuable first indications for fixed-bed systems but have to be handled with care because their applicability to a broad range of biomass fuels needs further investigations.

**Chemical fractionation** turned out to be an interesting tool to investigate the way how ash forming elements are bound in a biomass fuel. It can provide a more detailed image of fuel associations than e.g. a bulk ash chemical analysis and gives a preliminary idea on the reactivity of inorganic elements. However, restrictions regarding the direct practical interpretation of the results as well as the fact that this method is rather time consuming and expensive makes it more interesting for scientific studies than for industrial applications.

The same is true for **SEM/EDX analyses** of ashed fuels which provide, compared to bulk analyses the advantage that single ash particles can be investigated. Their application can be recommended for the investigation of specific phenomena as well as ash transformation processes (analyses of samples ashed at different temperatures). Regarding the characterisation of ashes, slags and deposits as well as for corrosion studies, the outstanding value of SEM/EDX analyses is indisputable since they provide the possibility to investigate single particles as well as different phases in a rather quick and accurate way. However, in the

course of advanced fuel characterisation these kinds of analyses can only be applied as a supporting tool for e.g. lab-scale reactor tests and not as a stand-alone procedure.

Also **thermodynamic equilibrium calculations (TEC)** have been evaluated as a valuable supporting tool in advanced fuel characterisation. Advantages of TEC are that they are rather cheap and quick, the software codes are in principle easy to use, they can provide detailed insights into ash chemistry and ash transformation processes and that they allow for the simulation of the behaviour of different ash fractions. However, TEC has to be used with care since the correct selection of the models as well as the thermodynamic databases applied may have a considerable influence on the results. These advantages make TEC, if carefully applied, a suitable method to derive trends and qualitative and sometimes semi-quantitative assessments. On the other hand there are certain restrictions and limitations given which do normally not allow for a quantitative prediction based on TEC. These restrictions and limitations are mainly related to the quality of the thermodynamic databases applied as well as to kinetic limitations which are not considered by TEC.

Also regarding the investigation of ash transformation and ash melting, **DSC** respectively **STA** measurements turned out to provide interesting qualitative results. The advantages of DSC analyses are that they can be performed with small samples of ashes or ashed fuels, that they are rather quick, show a good repeatability and can provide scientifically relevant data regarding chemical reactions, phase changes as well as ash melting behaviour. Relevant weaknesses and restriction to be mentioned are related to the sample pre-treatment (e.g. ashing of fuels and sample homogenisation) which may have an influence on the results. Therefore, DSC analyses are mainly performed in the course of scientific work as a supporting tool for e.g. thermodynamic equilibrium calculations regarding the behaviour of ash forming elements.

While the methods mentioned above can provide qualitative assessments of thermal conversion related problems of biomass fuels or deeper insights into specific aspects (e.g. ash chemistry), test runs at batchwise or continuously operated lab-scale reactors can result in quantitative data regarding thermal conversion, pollutant formation, aerosol and deposit formation, corrosion as well as ash related problems. In this respect the strengths of **special purpose built batch reactors** are that a rather small sample mass is needed and that the time demand for the experimental work is comparably low. Due to the possibility to adjust the settings and conversion conditions in batch reactors in a very controlled way, the data gained can typically be translated to real-scale processes. Moreover, they can provide valuable basic information for model development and validation. This can concern models to describe the biomass conversion process itself (e.g. fuel decomposition as well as char oxidation models) but also models to simulate NO<sub>x</sub>, particulate matter and deposit formation. However, the reactors usually applied are purpose built and therefore not commercially available. Moreover, well educated and experienced personnel is needed to operate the reactors.

**Continuously operated reactors** also show a huge potential for advanced fuel characterisation. In these reactors conditions of industrial processes can be reliably reproduced and therefore, the data are directly applicable to real-scale processes. Due to the continuous operation also long-term experiments including full mass balances as well as investigations regarding deposit formation and corrosion as well as bed agglomeration (for which typically extended test run durations are needed) are possible. Various analysers can be coupled to the reactors and therefore, a considerable number of different parameters can be measured and evaluated. Compared with the other methods mentioned, continuously operated reactors are

complex and test runs are more cost intensive. Moreover, the operation costs of the reactors are also considerable since not only electricity and in many cases natural gas but also experienced personnel are needed to run the systems.

Summing up, many different methods with significantly differing applicability are available for advanced biomass fuel characterisation. All these methods show their specific advantages and disadvantages and therefore, in many cases a combination of different methods is envisaged. It can generally be recommended to apply the evaluation of fuel indexes as a first step in fuel characterisation in order to gain a qualitative pre-evaluation of conversion related problems to be expected. In a second step, test runs in batchwise or continuously operated lab-scale reactors are recommended in order to gain quantitative data. The selection of the reactor, the test run setup as well as the measurement and analyses program has to be adjusted to the specific problems expected from the utilisation of the fuel (derived from the interpretation of fuel indexes) as well as the constraints of the process where it shall in future be applied. TGA, chemical fractionation, SEM/EDX analyses, STA-tests as well as TEC can be used as supporting tools to gain deeper insights into specific aspects as well as to gain basic data (e.g. kinetic data) for process modelling. If a new fuel has been positively evaluated by these methods with regard to an application in real-scale it is recommended to finally perform a pilot-scale test run with this fuel. Thereby, the plant settings can already be optimised based on the results gained from the advanced fuel characterisation.

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## **ANNEX A: Questionnaire regarding the provision of data and information sent out to the participating laboratories**

in cooperation with

## IEA Bioenergy, Task „Biomass Combustion and Co-firing“

Report on new fuel characterisation methods, summarizing the  
result of recent EU, ERANET and national projects

## Questionnaire regarding the application of advanced biomass fuel characterisation methods

Graz, October 2013

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### Biomass Combustion and Cofiring



## **Introduction and overall goal**

Biomass fuel characterisation is a relevant issue for all thermo-chemical conversion technologies. At present biomass fuel characterisation is mainly done by wet chemical or TGA analysis. Within the last years several national and international projects were initiated, which focus on advanced biomass fuel characterisation techniques in order to define the behaviour of a fuel during the pyrolysis, gasification and combustion stage as good as possible and thus support the proper design of a conversion plant. These efforts are of additional relevance since “new” biomass fuels come up which are not yet well characterised (e.g. short rotation coppice, energy grasses, biomass residues from industry as well as residues from pyrolysis and liquid biofuel production like char and hydrolytic lignin). These fuels usually contain elevated amounts of ash forming elements (especially of K), S, Cl as well as N. Consequently during their thermal conversion often problems with ash melting, deposit formation, corrosion as well as gaseous S-, Cl- and N-compounds occur. Sometimes they additionally show decomposition characteristics which significantly differ from conventional biomass fuels. As a consequence, advanced fuel characterisation methods are needed to make quick evaluations regarding these risks possible for a certain biomass fuel. By that way, the need for the performance of cost intensive real-scale trials can be minimised.

In recent years new advanced biomass fuel characterisation techniques based on the definition of fuel indices, thermodynamic equilibrium calculations regarding the behaviour of ash forming elements as well as lab-scale reactors have been developed respectively are under development. The latter focus on the characterisation of the release behaviour of NO<sub>x</sub> precursors and ash forming elements (e.g. K, Na, Zn, Pb, S, Cl) during the different conversion stages. Moreover, they are also used for the determination of conversion kinetics. Different lab-reactor designs are applied whereas the types of reactors (fixed bed, fluidised bed, single particle reactors, etc), the operation conditions (pyrolyses/gasification/combustion mode) as well as the sample intake and the kind of operation (batchwise or continuous operation) are manifold. Consequently, also the data that can be gained from tests at these different reactors vary significantly depending on the heating rates, atmospheres and reactor type applied.

However, all these advanced methods presently used or under development have their advantages as well as a certain application range. Therefore, an overview report about advanced biomass fuel characterisation techniques including a discussion of the strengths and weaknesses of the different methods, their specific fields of application as well as of already available results for selected biomass fuels gained with these methods shall be compiled.

## **Objectives of this questionnaire**

This questionnaire shall provide the basis for the evaluation of the current status concerning the development and application of advanced biomass fuel characterisation methods. To put the advanced fuel characterisation methods into an overall perspective also questions regarding conventional characterisation methods are contained in the first section of the questionnaire.

## Definitions

Conventional biomass fuels:	typical wood fuels (wood chips, bark, sawdust, wood pellets, etc.) which are commonly applied in thermal biomass conversion plants as well as straw
New biomass fuels:	all other biomass feedstocks such as for instance short rotation coppice, energy grasses, biomass residues from industry as well as residues from pyrolysis and liquid biofuel production like char and hydrolytic lignin
Advanced fuel characterisation tools:	techniques applied for biomass fuel characterisation which provide indications respectively detailed information regarding specific conversion related properties of a specific biomass fuel
Fuel properties of interest	List can be extended: <ul style="list-style-type: none"><li>• thermal decomposition at specified high heating rates</li><li>• volatiles and char content</li><li>• pyrolysis and gasification behaviour (kinetics)</li><li>• release of NO<sub>x</sub> pre-cursors</li><li>• release of easily volatile and semi-volatile inorganic elements</li><li>• potential for aerosol formation</li><li>• potential for ash deposit formation</li><li>• potential for high-temperature corrosion</li><li>• potential for HCl and SO<sub>x</sub> emissions</li><li>• ash melting behaviour</li></ul>

## 1. General questions

Does your institution have a standard strategy for biomass fuel characterisation?  yes  no

If yes briefly describe the strategy:

Is it generally applicable for biomass fuels or only for selected one?

## 2. Conventional biomass fuel characterisation

### 2.1. Proximate and ultimate analyses

Do you perform chemical fuel analyses by yourself?  yes  no

Do you contract chemical fuel analyses ?  yes  no

Which methods are usually applied for the following parameters  
(please enter either a standard or, if an in-house method is applied, a short description of the method)

volatiles content

char content

moisture content

ash content

C

H

N

S

Cl

major ash forming elements

minor ash forming elements

ash melting behaviour



### 3. Advanced fuel characterisation

#### 3.1. Fuel indexes

Do you apply fuel indexes to evaluate conversion related fuel properties?  yes  no

If yes please briefly describe the index as well as its application  
(example: index: molar ratio of 2S/Cl; description: indicates potential for high-temperature chlorine corrosion; <2: high corrosion risk; >8: low corrosion risk)

index:

application:

index:

application:

index:

application:

#### **Method assessment**

---

How do you assess the applicability of fuel indexes for advanced biomass fuel characterisation?

---



Strengths:

Weaknesses:

Restrictions:

Other comments:

**Please add related publications if available to ANNEX I**

### 3.2. Advanced wet chemical analyses methods

Do you apply advanced analyses methods such as for instance chemical fractionation?  yes  no

If yes please briefly describe the method

Method:

Description:

#### ***Method assessment***

---

	😊							☹️
How do you assess the applicability of advanced wet chemical analyses methods for advanced biomass fuel characterisation?	<input type="checkbox"/>							

---

Strengths:

Weaknesses:

Restrictions:

Other comments:

***Please add related publications if available to ANNEX I***

### 3.3. Advanced methods based on SEM/EDX

Do you apply advanced analyses methods based on SEM/EDX ?

yes  no

If yes please briefly describe the method

Method:

Description:

#### ***Method assessment***

---

How do you assess the applicability of advanced methods based on SEM/EDX for advanced biomass fuel characterisation?

---



Strengths:

Weaknesses:

Restrictions:

Other comments:

***Please add related publications if available to ANNEX I***

### 3.4. Thermodynamic high temperature equilibrium calculations (TEC)

Do you apply (TEC) for the prediction of ash related properties?  yes  no

If yes

for the investigation of the ash melting behaviour  yes  no

for the investigation of inorganic element release  yes  no

for other purposes (list which)

software applied:

databases applied

#### **Method assessment**

How do you assess the applicability of TEC regarding	☺				☹
investigation of the ash melting behaviour	<input type="checkbox"/>				
investigation of inorganic element release	<input type="checkbox"/>				
other applications	<input type="checkbox"/>				

Strengths:

Weaknesses:

Restrictions:

Other comments:

**Please add related publications if available to ANNEX I**

### 3.5. Differential scanning calorimetry (DSC)

Do you apply DSC for the investigation of ash related properties (e.g.: ash melting behaviour)?  yes  no

If yes please continue

Equipment

DSC equipment (supplier, model)

Test procedure

atmosphere (inert, oxidising, etc.)

heating rate (K/min)

temperature range from °C to °C

heating ramp

sample intake (mg)

Evaluation of results

parameters investigated

#### **Method assessment**

---

How do you assess the applicability of DSC for advanced biomass fuel characterisation? ☺ ☹

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Strengths:

Weaknesses:

Restrictions:

Other comments:

**Please add related publications if available to ANNEX I**

### 3.6. Special purpose built lab-scale batch reactors

#### 3.6.1. Reactor name:

Examples: single particle reactors, heated grid reactors, macro-TGA

Do you apply such a special reactor for fuel characterisation?

yes  no

If yes, is it an in-house development

yes  no

If no, the supplier is

Description of the device

reactor type (single particle, heated grid etc.)

brief description of the set-up

shape (cylindrical, cubic, etc.)

diameter (hydraulic)

lengths

material (inner lining of the reaction zone)

sample intake (g)

heating strategy (e.g.: directly, indirectly, heating medium)

heating rate

operation temperature range (°C)

reaction medium (e.g.: N<sub>2</sub>, air, etc.)

Analysers and measurement equipment coupled to the reactor

balance  yes  no

gas analysers  yes  no

if yes, indicate the compounds determined:

fuel analyses  yes parameters

ash analyses  yes parameters

Please briefly describe the testing protocol:

Parameters investigated:

decomposition behaviour  yes  no

kinetics  yes  no

char formation  yes  no

mass loss during conversion  yes  no

fuel temperature  yes  no

flue gas composition  yes  no

NO<sub>x</sub> precursor release  yes  no

inorganic element release  yes  no

other parameters

special features

**Method assessment**

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😊 ☹️

How do you assess the applicability of the reactor described for advanced biomass fuel characterisation?

---

Strengths:

Weaknesses:

Restrictions:

Other comments:

***Please add related publications if available to ANNEX I***

***For the description of additional reactors please contact Dr. Thomas Brunner ([brunner@bios-bioenergy.at](mailto:brunner@bios-bioenergy.at)) and tell him the number of reactors you would like to add. He will then send you an appropriate questionnaire.***

### 3.7. Special purpose built continuously working reactors

#### 3.7.1. Reactor name:

Examples: drop tubes, entrained flow reactors, fluidised bed reactors

Do you apply such a special reactor for fuel characterisation?  yes  no

If yes, is it an in-house development  yes  no

If no, the supplier is

#### Description of the device

reactor type (e.g. entrained flow, fixed bed fluidised bed)

brief description of the set-up

shape (cylindrical, cubic, etc.)

diameter (hydraulic)

lengths

material (inner lining of the reaction zone)

heating strategy (e.g.: directly, indirectly heated, specify heating medium)

input material particle size  pulverfised  pellets  chipped

thermal capacity (fuel power related to NCV) from kW to kW

sample flow (kg/h)

process temperature from °C to °C

wall temperature from °C to °C

operation pressure  atmospheric  pressurised up to bar

reaction medium (e.g.: N<sub>2</sub>, air, etc.)

#### Analysers and measurement equipment coupled to the reactor

balance  yes  no

gas analysers  yes  no

if yes, indicate the compounds determined:

other measurements (e.g. deposit probes)

fuel analyses  yes parameters

ash analyses  yes parameters

#### Possible investigations with the reactor

devolatilization tests  yes  no

pyrolyses tests  yes  no

gasification tests  yes  no

combustion tests  yes  no

#### Information gained from test runs

decomposition behaviour  yes  no

kinetics  yes  no

char formation  yes  no

flue gas composition  yes  no

NO<sub>x</sub> precursor release  yes  no

inorganic element release  yes  no

deposit formation  yes  no  
gaseous emissions  yes  no  
particulate emissions  yes  no  
other parameters  
special features

**Method assessment**

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☺ ☹

How due you assess the applicability of the reactor described for advanced biomass fuel characterisation?

---

Strengths:

Weaknesses:

Restrictions:

Other comments:

*Please add related publications if available to ANNEX I*

**For the description of additional reactors please contact Dr. Thomas Brunner ([brunner@bios-bioenergy.at](mailto:brunner@bios-bioenergy.at)) and tell him the number of reactors you would like to add. He will then send you an appropriate questionnaire.**

### 3.8. Other methods / equipment

#### 3.8.1. Method / equipment name:

Please describe any other methods or equipment you apply following the structure below

Name of method/equipment

Description of the method/device

Please briefly describe the testing protocol:

Parameters investigated:

#### **Method assessment**

---

How do you assess the applicability of the method/equipment described for advanced biomass fuel characterisation?

---



Strengths:

Weaknesses:

Restrictions:

Other comments:

**Please add related publications if available to ANNEX I**

**For the description of additional methods/equipment please contact Dr. Thomas Brunner ([brunner@bios-bioenergy.at](mailto:brunner@bios-bioenergy.at)) and tell him the number of reactors you would like to add. He will then send you an appropriate questionnaire.**

## **ANNEX 1 – related publications**

Please add references if available

Please attach pdf-files with the respective publication(s) (if available)

**Please consider the deadline for the submission of the filled in questionnaire: end of February 2014**