



TECHNISCHE
UNIVERSITÄT
WIEN

Vienna University of Technology

Dissertation

Properties and slagging behaviour of ashes from small-scale biomass combustion

ausgeführt zum Zwecke der Erlangung des akademischen Grades einer
Doktorin der technischen Wissenschaften unter der Leitung von

Hermann Hofbauer

E166 Institut für Verfahrenstechnik, Umwelttechnik
und Technische Biowissenschaften

eingereicht an der Technischen Universität Wien
Fakultät für Maschinenwesen und Betriebswissenschaften
von

Elisabeth Wopienka

e9400736

Bahnhofstrasse 18/2/16,
3250 Wieselburg

Wien, am 28. Oktober 2014

Kurzfassung

Die zunehmende Nutzung von Biomassebrennstoffen für die Wärmebereitstellung führt zu einem entsprechenden Anstieg bei der Nachfrage an Holz, und somit auch zu einem steigenden Wettbewerb um diesen Rohstoff mit anderen Industriebereichen. Für die Produktion von Biomassebrennstoffen werden daher zunehmend alternative Rohstoffe in Betracht gezogen – z. B. geringerwertige Holzqualitäten, Energiepflanzen oder landwirtschaftliche Nebenprodukte. Die daraus resultierende große Bandbreite an Brennstoffeigenschaften stellt Feuerungshersteller vor große Herausforderungen – besonders im Bereich der Kleinfeuerungsanlagen. Ein zentraler Punkt diesbezüglich sind niedrige Ascheschmelztemperaturen und folglich Schlackebildung im Rostbereich. Eine Ausweitung der Datenbasis sowie Erfahrungswerte betreffend die Verschlackungsneigung in realen Anwendungen stellen eine wichtige Grundlage zum Einen für die Festlegung sinnvoller Qualitätskriterien und dementsprechende Optimierung der Brennstoffqualität, und zum Anderen für eine diesbezügliche Weiterentwicklung von Feuerungen dar.

In der vorliegenden Arbeit wurden Ascheschmelzverhalten und Verschlackungsneigung verschiedener Biomassebrennstoffe untersucht, wobei der Fokus auf Schlackebildung im Rostbereich von Kleinfeuerungsanlagen lag. Dabei wurden brennstoffseitige wie auch feuerungsseitige Maßnahmen zur Verringerung der Schlackebildung berücksichtigt, und Möglichkeiten für eine geeignete Bewertung oder Klassifizierung der großen Bandbreite an Biomassebrennstoffen hinsichtlich deren Verschlackungsneigung analysiert.

Unterschiedliche Brennstoff- und Ascheproben wurden analysiert, und Ergebnisse mittels multivariater statistischer Methoden ausgewertet. Verbrennungsversuche dienten der Untersuchung der praktischen Verschlackungsneigung, wobei eine Vielzahl unterschiedlicher Holzbrennstoffe sowie auch verschiedene nicht-holzartige Biomassen eingesetzt wurden (z. B. Stroh, Mais Ganzpflanze, Miscanthus oder Heu). Unterschiedliche Feuerungstechnologien im kleinen Leistungsbereich kamen zur Anwendung, um auch technologische Einflussfaktoren auf die Bildung von Verschlackungen zu untersuchen. Darüber hinaus wurden verfügbare Methoden zur Bewertung des Ascheschmelzverhaltens bzw. der Verschlackungsneigung analysiert, und Ansatzpunkte für eine entsprechende (Weiter-)entwicklung solcher Methoden erarbeitet.

Rohstoffart und -qualität wurden als die einflußreichsten Parameter hinsichtlich Ascheschmelzeigenschaften bestätigt, und lassen vor allem für holzartige Biomassen eine Ableitung entsprechender Optimierungsmaßnahmen zu. Gezieltes Mischen von Rohstoffen oder die Beimengung mineralischer Additive erwiesen sich als potentiell hilfreiche Maßnahmen, deren Sinnhaftigkeit und Effektivität jedoch im Einzelfall zu prüfen ist. Betreffend die Verbrennungstechnologie wurden grundlegende Anforderungen an Feuerungsdesign und Anlageneinstellungen benannt, welche beim Einsatz schlackebildender Brennstoffe zu berücksichtigen sind. Als zentrale Elemente wurden diesbezüglich die Verfügbarkeit von ausreichend Platz im Rostbereich und regelmässige Bewegung des Glutbetts identifiziert, und auch kürzere Verweilzeiten der Brennstoffrückstände in der Verbrennungszone wurden als vorteilhaft bewertet.

Der Aschegehalt erwies sich innerhalb des gesamten Spektrums an Biomassebrennstoffen als weniger bedeutender Einflussfaktor, welcher allenfalls als Qualitäts-Indikator innerhalb derselben Rohstoffart herangezogen werden kann – z. B. zum Vergleich von Holzbrennstoffen. Auch auf Basis der charakteristischen Temperaturen des Ascheschmelztests (DIN 51730) waren keine zuverlässigen Schlussfolgerungen hinsichtlich der praktischen Verschlackungsneigung möglich.

Ein signifikanter Zusammenhang von Elementarzusammensetzung und Ascheschmelzverhalten konnte bestätigt werden, und Si, Al, K, P, Ca und Mg wurden diesbezüglich als die wichtigsten Elemente identifiziert. Vorhersagewerte für konkrete Schmelztemperaturen aus empirischen Gleichungen auf Basis von Elementkonzentrationen wiesen jedoch beträchtliche Fehlerbereiche auf – sowohl bei Anwendung verfügbarer Gleichungen aus der Literatur auf eigene Daten, als auch für ein im Rahmen der Arbeit entwickeltes Regressionsmodell. Eine derartige Berechnung konkreter Temperaturen zur praktischen Brennstoffbewertung wurde daher als nicht zielführend erachtet. Eine Einschätzung mit Hilfe von Brennstoffindices, sowie ein Versuch der Klassifizierung der Analysendaten mit Hilfe multivariater Statistikmethoden auf Basis der Elementarzusammensetzung zeigte gute qualitative Übereinstimmung mit praktischen Ergebnissen und Entwicklungspotential.

Ein Vergleich charakteristischer Temperaturen aus dem Ascheschmelztest mit praktischen Versuchsergebnissen enthüllte den dringenden Bedarf an verbesserten oder neuen Charakterisierungsmethoden, um relevante und verlässliche Informationen bezüglich der Verschlackungsneigung von Biomassebrennstoffen zu generieren, und weiters eine Unterscheidung bzw. Einstufung problematischer und unproblematischer Brennstoffqualitäten zu ermöglichen. Auch Anforderungen an eine solche Methode wurden spezifiziert.

Abstract

The recent rise in use of biomass fuels for heat production consequently produces a higher demand of wood at the fuel market, where due to limited availability of economically priced wood, the market for alternative biofuels is growing rapidly, and woody materials of lower quality as well as agricultural raw materials and residues are considered in this regard. The resulting increase in variability of fuel properties poses a major challenge to boiler manufacturers – in particular in the field of small-scale applications, and ash melting and slag formation in the grate section are of major relevance in this regard. A comprehensive database of ash melting properties of different types of biomass as well as information about the slagging behaviour in real applications are essential for defining reasonable quality criteria for solid biomass fuels to this effect. Moreover, a respective knowledge facilitates the optimisation of biomass fuel qualities as well as further development of combustion technologies.

In the present thesis, ash melting and slag formation of various types of biomass are investigated, focusing on slag formation in the grate section of small-scale combustion appliances. In this regard, fuel- and technology related measures to reduce slag formation are studied. Furthermore, possibilities for an adequate assessment or classification of the wide range of biomass fuels with respect to their slag formation tendency are analysed.

A number of different fuel and ash samples were analysed, and results were evaluated via multivariate statistical methods. Combustion tests for an evaluation of the practical slagging performance were conducted, and a broad variety of wood pellets but also various types of non-woody biomass fuels like e.g. straw, Miscanthus, maize whole crop or hay were tested. Different small-scale combustion technologies were used in order to investigate influencing factors on slag formation from the technological point of view. A literature study on analyses methods for the characterisation of ash melting properties additionally supports the interpretation of findings and respective conclusions.

Nature and quality of the raw material were confirmed as the most decisive factor with regard to ash melting properties, and possibilities for a respective optimisation of the fuel quality are more easy to realise for woody than for non-woody biomass fuels. Blending raw materials or using additives was found to be potentially effective in this regard, but careful consideration was recommended for individual cases. Moreover, several requirements were defined regarding design and settings of small-scale combustion appliances suited for slagging fuels.

In view of the large range of biomass fuels, the ash content was found to be of minor relevance with regard to the severity of slag formation, and may only be used as an indicator of fuel quality among similar fuel types – e.g. for woody raw materials. Furthermore, no quantitative information about the practical slag formation tendency was obtained from characteristic temperatures of the standard ash fusion test (DIN 51730).

Significant correlation of elemental composition and ash melting behaviour was confirmed, and Si, Al, K, P, Ca and Mg were identified to be the most relevant elements in this regard. No reasonable prediction of characteristic melting temperatures was verified – neither using

existing methods nor based on an own developed regression model. However, good accordance with ash melting properties was found for both evaluation of biomass fuels based on fuel indices and classification using multivariate statistical methods, which could be further improved.

A comparison of fuel analyses and results from practical combustion tests showed an urgent need of a new characterisation method that provides significant and reliable information on the slag formation tendency, and in particular facilitates differentiation from and grading of problematic fuel qualities, and major requirements for such a lab test method were summarised.

Danksagung

Ein Großteil der vorliegenden Arbeit entstand aus Forschungsprojekten der BIOENERGY 2020+ GmbH (vormals Austrian Bioenergy Centre GmbH), welche im Rahmen des COMET-Programms (früher *Kplus*-Programm) von der Österreichischen Forschungsförderungsgesellschaft gefördert wird. Großer Dank gebührt diesbezüglich DI Dr. Walter Haslinger sowie DI Dr. Günther Friedl welche maßgeblich zum Zustandekommen dieser Projekte beigetragen haben.

Mein besonderer Dank gilt Herrn Univ.-Prof. Dipl.-Ing. Dr. Hermann Hofbauer für die Betreuung meiner Dissertation, und die gewissenhafte Auseinandersetzung – sowohl Inhalte und größere Zusammenhänge betreffend, als auch im Hinblick auf kleine Details. Auch möchte ich Prof. Marcus Öhman für die externe Begutachtung der Arbeit, sowie für kritische Anregungen und motivierende Gespräche rund um das Thema „Biomasseaschen und Verschlackungsneigung“ im Zuge gemeinsamer Projektarbeiten danken.

Bedanken möchte ich mich auch bei DI Dr. Günther Friedl welcher mir vor allem in der Anfangsphase der Arbeit geholfen hat, Struktur in das Thema zu bringen, sowie bei DI Dr. Bettina Liebmann, welche mir bei einigen Fragen der multivariaten Datenanalyse mit Rat zur Seite gestanden ist.

Besonders dankbar bin ich meinen Kolleginnen und Kollegen Ing. Mag. (FH) Franz Figl, Mag. (FH) Dr. Gottfried Eder, DI Matthias Heckmann, DI (FH) Christian Pointner, Eng. MSc. Lara Carvalho und DI Waltraud Emhofer welche an den für diese Dissertation relevanten Projekten mitgearbeitet haben – vor allem für die gut nachvollziehbare und ausführliche Projektdokumentation, und die hohe Qualität ihrer Arbeitsbeiträge, welche mir das Arbeiten sehr oft erleichtert haben.

Eine große Unterstützung beim Verfassen dieser Arbeit war das Arbeitsumfeld bei BIOENERGY 2020+ GmbH – vor allem die Möglichkeit zur Wiederaufnahme der Arbeiten und des Arbeitsthemas nach Rückkehr aus Karenz, sowie flexible Arbeitsbedingungen. Darüber hinaus sind vor allem der wertschätzende Umgang und ein sehr freundschaftliches Verhältnis mit vielen Kolleginnen und Kollegen für mich von unschätzbarem Wert. Besonderer Dank gilt an dieser Stelle dem unermüdlichen Kernteam der Dissertationsgruppe – Waltraud, Manuel und Babette – als wichtige moralische Unterstützung beim Fertigstellen meiner Dissertation.

Ein herzlicher Dank gilt nicht zuletzt meiner Familie und meinen Freunden, die auf ihre Art und Weise sehr zum Gelingen dieser Arbeit beigetragen haben.

Table of contents

1	INTRODUCTION	1
2	OBJECTIVES AND APPROACH.....	3
3	STATE OF THE ART AND LITERATURE REVIEW	5
3.1	Solid biofuels for small-scale combustion units.....	5
3.1.1	Raw materials for solid biofuel production	5
3.1.2	Fuel properties and quality standards	6
3.2	Automatically stoked small-scale combustion units.....	8
3.2.1	Combustion principles	9
3.2.2	Grate systems and ash removal solutions	10
3.3	Principles of ash and slag formation from biomass combustion	12
3.3.1	Ash forming elements.....	12
3.3.2	Mechanisms of ash and slag formation in biomass combustion	15
3.3.3	Release of ash forming elements.....	20
3.3.4	Ash fractions from fixed bed biomass combustion.....	25
3.3.5	Measures to improve ash melting properties of biomass fuels	26
3.4	Methods to assess the ash melting behaviour.....	28
3.4.1	Evaluations based on elemental composition	30
3.4.2	Laboratory methods	32
3.4.3	Experimental evaluation in small-scale combustion units	36
4	MATERIALS AND METHODS	37
4.1	Fuels	37
4.2	Combustion units	40
4.3	Experimental set up and program	43
4.3.1	Test procedure	43
4.3.2	Description of test series	44
4.4	Evaluation of ash and slag	46
4.4.1	Terminology of combustion residues	46
4.4.2	Ash and slag sampling	46
4.4.3	Assessment of slag formation	47
4.5	Methods for fuel and ash analysis.....	48
4.6	Determination of elemental release.....	49

4.7	Terms and definitions of descriptive statistics	50
4.8	Multivariate data analysis	51
4.8.1	Terms and methods in multivariate data analysis	51
4.8.2	Algorithms and settings used in multivariate data analysis	52
5	RESULTS AND DISCUSSION	55
5.1	Property related biomass classification.....	56
5.1.1	Basic information on exploratory data analysis.....	56
5.1.2	Distances and similarities – groups of similar properties	56
5.1.3	Discussion	60
5.2	Variability of ash composition and elemental release	63
5.2.1	Ash composition of different fuels	63
5.2.2	Variation among ash fractions and sampling positions	66
5.2.3	Influence of combustion conditions on the bottom ash composition	67
5.2.4	Influence of fuel composition on elemental release	73
5.2.5	Discussion	75
5.3	Comparing laboratory ashes and ashes from combustion processes.....	78
5.3.1	Elemental composition of laboratory ashes and ashes from combustion appliances.....	78
5.3.2	Ash melting behaviour of laboratory ashes and ashes from combustion appliances	84
5.3.3	Discussion	86
5.4	Fuel related influencing factors on ash melting and slag formation	87
5.4.1	Ash melting and slag formation of different types of biomass	87
5.4.2	Variation and improvement of wood pellets	93
5.4.3	Effect of additives	106
5.4.4	Discussion	113
5.5	Technology related aspects on slag formation	120
5.5.1	Wood pellets fired in different combustion units.....	120
5.5.2	Different types of boilers tested with non-woody biomass fuels	123
5.5.3	Air supply in the combustion zone.....	126
5.5.4	Agitation of the fuel bed and grate cleaning intervals	130
5.5.5	Discussion	132
5.6	Theoretical approaches to determine the ash melting behaviour.....	136
5.6.1	Applicability of available equations to own biomass data	136
5.6.2	Practical slagging performance versus theoretical indices	142
5.6.3	Effect of additive utilisation	144
5.6.4	Modelling melting temperatures via multivariate calibration	146
5.6.5	Discussion	149
5.7	Theoretic examination of laboratory methods for the determination of ash melting properties	152
5.7.1	Aspects on relevance and applicability	152
5.7.2	Performance of different methods	157

5.7.3	Relevance of test results with regard to practical slagging behavior in small-scale combustion.....	159
5.7.4	Discussion	160
6	SUMMARY AND CONCLUSIONS	162
6.1	Fuel related possibilities to reduce slag formation	162
6.2	Requirements for small-scale combustion appliances suited for slagging fuels	163
6.3	Relevance of conventional fuel parameters with regard to practical slagging performance 164	
6.4	Classification of biomass fuels with regard to slagging properties	165
6.5	Requirements for a lab test method to assess the slag formation tendency of biomass fuels 166	
7	KEY FINDINGS AND FUTURE PROSPECTS	167
8	REFERENCES	170
9	ANNEX I – ABBREVIATIONS AND LIST OF SYMBOLS	179
10	ANNEX II – LIST OF TABLES	181
11	ANNEX III – LIST OF FIGURES	183
12	ANNEX IV – PROPERTIES OF FUEL AND ASH SAMPLES	186

1 Introduction

Solid biomass for energy production

The EU climate and energy strategy for 2020 is summarized in the 20-20-20 targets, thus setting three key objectives: Reducing the EU greenhouse gas emissions by 20 % from 1990 levels, raising the share of EU energy consumption produced from renewable resources to 20 % and improving the EU's energy efficiency by 20 % until 2020 [Directive 2009/28/EC]. The use of renewable energy sources is of major relevance in this regard along with increase in efficiency and energy saving. Moreover, activities in these fields additionally support objectives of the Europe 2020 strategy, by promoting technological development and innovation, increasing the security of energy supply and providing opportunities for employment and regional development.

The heating sector plays a major role on the energy market. Currently about 50 % of the primary energy production is used for heat production, and 50 % of the final energy consumption in the EU is heat. Thus, the utilisation of biomass for heat production has the potential for considerable contributions to the EU 2020 targets.

Due to high costs and an unstable market for fossil fuels as well as political directives pushing the use of CO₂-neutral energy sources, the use of renewable energy sources for heat production has increased significantly during the past years. As a consequence a considerable market has evolved in the field of biomass combustion, in particular companies producing or merchandising solid biofuels as well as boiler manufacturers.

Widening the raw material base for biomass fuels and respective challenges

The market for biomass combustion systems for residential heating has increased significantly during the last years. In Austria e.g. the number of newly installed pellets combustion units has increased from around 1 000 in 1998 and 5 000 in 2003 to more than 10 000 units per year in 2013. Also a continuous increase is found for wood chip boilers until 2005, since then showing variations between 3 000 and 4 000 newly installed appliances per year. [HANEDER 2014]

The rise in energy production from biomass consequently produces a higher demand of wood at the fuel market, where increasing competition with other sectors of industry can be observed. Due to limited availability of economically priced wood, the market for alternative biofuels is growing rapidly, and woody materials of lower quality as well as agricultural raw materials and residues are considered in this regard. Moreover, the market for combustion technologies has expanded over all European countries, where boiler manufacturers are faced with other raw materials or raw material qualities.

Combustion technologies need to be designed for particular fuel qualities in order to provide for good combustion quality. Thus, the broad variety of properties of solid biofuels may lead to considerable problems as to the combustion process in terms of increased emissions, corrosive attack or ash melting and slag formation in the grate section. Moreover, available methods are inadequate to characterise the whole range of biomass fuels in this regard.

Ash melting and slag formation in residential biomass combustion

Ash melting and slag formation in the grate section of residential biomass boilers has occasionally been observed for wood pellets, and incidents are more frequently found for lower wood pellet qualities. Moreover, slag formation occurs during combustion of most non-woody biomass fuels.

Slag is formed by low-melting ashes or ash-fractions respectively, and accumulation of resulting ash or slag lumps in the grate section may considerably affect the combustion process. Reducing access and circulation of combustion air, inhibiting the supply with fresh fuel and the discharge of combustion residues respectively or blocking moving parts of the boiler are potential implications, thus leading to increased emission values or even a shutdown of the boiler. Moreover, corrosive attack e.g. on refractory material components is possible.

The ash fusion test is the only standardised method currently available for the description of the ash melting properties of solid biofuels, but the significance and applicability of this method for a wide range of biomass fuels is frequently doubted (more detailed information on that issue is provided in sections 5.7.2 and 5.7.3). In addition, numerous theoretical and lab test methods have been developed for the assessment of biomass fuels in this regard, but none of them has been comprehensively applied so far. However, the missing link is the evaluation of the significance of any lab test method relating to and in comparison with the performance of a respective fuel in real combustion appliances.

Requirements to advance in ash melting characterisation of solid biomass fuels

In view of the broad variety of solid biomass fuels, the database on fuel properties still needs to be amplified to gain knowledge regarding groups showing similar slag formation behavior, at most allowing for a respective classification.

Influencing factors on slag formation need to be identified as well as graded regarding the extent of their respective impact, thus facilitating to take appropriate measures to reduce slag formation in small-scale combustion appliances. Both fuel related and technology related aspects need to be considered in this regard.

Moreover, an adequate characterisation method needs to be specified, that provides reliable and reproducible results for the whole range of solid biomass fuels. A method with regard to ash melting properties and slag formation tendency under real application conditions is of major relevance in this regard.

Subject of the present thesis is to investigate properties of different types of biomass ashes as well as their melting and slagging behavior in small-scale combustion units, focusing on a respective characterization and classification and potential measures to reduce slag formation.

2 Objectives and approach

Objectives

The objective of this work is to investigate ash melting and slag formation on the grate and in the combustion zone of small scale biomass combustion units. Properties and variability of biomass ashes are investigated in this regard. Influencing factors on slag formation are examined considering both fuel related factors and aspects regarding the combustion technology. Moreover, methods and approaches for the assessment or grading of melting properties and in particular practical slagging behaviour of biomass ashes are studied.

These overall objectives include the following components:

Characterisation of ash and slag from small-scale biomass combustion

Typical properties like e.g. chemical composition or characteristic melting temperatures of ashes from different types of biomass are analysed. Moreover, the variability of biomass-, ash- and slag-composition is investigated, and properties of laboratory ashes and ashes from combustion experiments are compared.

Identification of the main influencing factors on slag formation in small scale biomass combustion

The impact of several fuel related parameters on the ash melting behaviour is evaluated. In this regard, a variety of woody and non-woody biomass fuels is considered, and also the effect of mineral additives is investigated. Moreover, technology related factors are discussed, considering design aspects (e.g. type and size of the grate) as well as combustion conditions or boiler settings (e.g. air supply or grate cleaning intervals).

Specification of the main issues concerning fuel classification

In view of more fuel flexibility and an increasing variation of fuel properties, ideas for an extended characterisation and related classification of solid biofuels regarding their slag formation propensity are developed. Therefor in particular aspects concerning the practical relevance of the results are discussed.

Identification of requirements regarding small-scale combustion technologies for slagging fuels

Analysing how different combustion technologies cope with slagging fuels, the major technology related factors determining the impact of slag formation on the combustion performance are identified. Consequently basic requirements for small-scale appliances operated with high ash and low ash melting fuels are specified.

Evaluation of theoretical approaches and characterisation methods for the assessment of the ash melting behaviour

Empirical equations and indices intended to describe ash melting properties or practical slag formation tendency are examined, and in addition an own model is developed. Moreover, advantages and disadvantages of available characterisation methods are presented, and their

comparability with real combustion conditions is discussed. Results from the ash fusion test (AFT) are compared to findings from practical combustion tests.

Approach

Experimental work close to real application

One main issue of the thesis is to investigate the practical slag formation tendency, i.e. observations or disturbances that would also be observed in real application. Therefore, combustion experiments are conducted in state of the art combustion units, and only minor changes with regard to boiler design or settings are allowed. Apart from specially produced fuels for systematic investigations, a number of samples from the market are tested.

Linking fuel data and theoretical approaches to practical results

Results from various theoretical approaches, fuel analyses and characteristic temperatures from the standard ash fusion test are interpreted and evaluated against the background of the slagging performance determined in practical combustion tests. Interpretation and conclusions focus on the practical slagging performance.

Compilation and evaluation of data from literature

Characterisation methods regarding the melting properties of fuel ashes are surveyed, and findings about advantages and disadvantages as well as the comparability of these methods are compiled from literature. In addition, equations and critical numbers found in literature are applied to own biomass data.

3 State of the art and literature review

Basic information on small-scale biomass combustion and ash related issues are outlined, focusing on aspects which are considered to be most relevant with regard to the scope of the thesis. Therefore, basic information is summarised and major output of previous investigations is presented.

Potential raw materials for solid biomass fuels are described, and relevant fuel properties and the respective standards are specified. Moreover, an overview about combustion principles as well as grate systems and ash removal solutions for automatically stoked small-scale combustion appliances is provided.

Information on ash forming elements is summarized, and the major transformation processes and chemical reactions are described, as well as the resulting ash and slag forming compounds. In this regard also the release of inorganic elements from the bottom ash and the main influencing factors in this regard are considered. Moreover, measures to improve ash melting properties of biomass fuels are discussed, and available methods for assessing the ash melting behavior are compiled.

3.1 Solid biofuels for small-scale combustion units

Different conversion pathways are available for energy production from biomass, based on thermal, chemical or biochemical processes, and different types of biomass are applicable for particular conversion technologies according to the respective fuel properties. Oil- or starch-containing biomass is usually processed, and the resulting products (e.g. oil, biogas or ethanol) are used for energy production.

Energy products like e.g. vegetable oil, biodiesel or ethanol are produced from oil- or starch-containing biomass (e.g. seeds of sunflower, rape or hemp and sugar beet or cane), whereas lignocellulosic biomass material (like e.g. wood, Miscanthus or straw) is usually directly used as a fuel for combustion or thermal gasification. According to the topic of the present work, only raw materials for solid biomass combustion are considered in the following section, providing an overview about potential raw materials and quality standards for solid biomass fuels.

3.1.1 Raw materials for solid biofuel production

Automatically stoked small-scale combustion appliances are usually operated with wood chips or pellets, and also small briquettes are sometimes used. However, the high demand of wood for solid biofuel production has induced increasing competition with other sectors of wood-processing industry. Due to the limited availability of economically priced wood, increasing interest for alternative biofuels was observed during the last decade. Consequently also woody materials of lower quality like e.g. vine pruning, bark, logging residues, wood from roadside maintenance or even waste wood are taken into account. Moreover, apart from woody materials also purpose-grown energy plants as well as by-products and residues from agriculture and the respective processing industries are investigated as to their applicability

as a biomass fuel. An overview about the potential of non-woody raw materials for solid biomass fuel production in different European regions is given in Table 1.

Table 1: Non-woody biomass identified as potential raw materials for fuel production in different European countries (i.e. Austria, Denmark, Finland, Germany, Italy, Spain and Sweden) classified according to the origin of the raw material. [KRISTÖFEL 2012]

Origin of the raw material	Type of raw material
Whole plant	Miscanthus, hemp, maize whole crop, grain, reed canary grass, hay (from landscape gardening)
Agricultural by-products	Rape straw, cereal straw, corn cob residues, cereal spilling almond hull, olive stones, corn stalks
Residues from industry	mash, marc, olive cake, rape press cake

Raw material classification

Solid biomass fuels are usually classified according to the raw material source (e.g. wood, grasses or cereal crops) or origin discriminating virgin material from forestry or agricultural production, by-products, residues or waste material from wood/herbaceous biomass/fruit processing industry, residues from landscape gardening or waste material (cf. KALTSCHMITT 2009, MARUTZKY 1999, HARTMANN 2013).

According to ÖNORM EN 14961-1 biomass fuels are primarily assigned to one of the main origin-based groups of solid biofuels, i.e.

- Woody biomass (biomass from trees, bushes and shrubs)
- Herbaceous biomass (biomass from plants that have a non-woody stem and which die back at the end of the growing season, including grains and their by-products such as cereals)
- Fruit biomass (biomass from the parts of a plant which are from or hold seeds)
- Biomass blends and mixtures (material of various s origin from one of the above mentioned groups; blends are intentionally mixed biofuels, whereas mixtures are unintentionally mixed biofuels)

Further differentiation within these groups is done according to the raw material source, stating whether the biomass is a virgin material, a by-product or a residue from industry.

The resulting groups are further divided into third and fourth level sub-groups, considering the type of plant (e.g. grasses, cereal crops, flowers) and also plant parts (e.g. whole plant, straw parts, grains or seeds), thus allowing for a detailed specification and differentiation of biofuel material. [ÖNORM EN 14961-1]

3.1.2 Fuel properties and quality standards

The variety of biomass raw materials shows considerable variations as to particular fuel properties. Information on e.g. dimensions, (bulk) density, calorific value, water content, ash content or concentrations of particular elements are of significant importance with regard to

storage and transport issues as well as combustion behaviour. Therefore, a respective classification and standardisation of biomass fuels is required.

Product standards are the basis for good understanding between seller and buyer as well as for communication between fuel producers and various equipment manufacturers. Moreover, they facilitate authority permission procedures and reporting, and are therefore essential for efficient trading as well as development of the market sector of biomass energy. [ÖNORM EN 14961-2]

Since 2011 European standards are available describing fuel specifications and classes for different types of solid biomass fuels like e.g. wood chips, log wood, pellets or briquettes [ÖNORM EN 14961-1-6], and the respective ISO standards are expected to be finalised by the beginning of 2014 [Wojcik 2013]. Table 2 exemplarily provides an overview about the specification for wood pellets according to ÖNORM EN 14961-2 as well as requirements and threshold values of previous national standards. Even though these standards have already been replaced by the European standard, they are shown for means of comparison, somehow representing the development and state of the art of biofuel production and common combustion appliances in a particular country.

The most significant differences among standards and quality classes are found regarding the threshold values for ash content as well as limits for nitrogen and sulphur. The most demanding threshold values for ash content are specified in former Austrian and German standards (ÖNORM M 7135 (HP 1), DINplus), and comparably high values are found in the respective French standards. Moreover, the grading of different property classes according to ÖNORM EN 14961-2 is mainly represented by the limits for ash and nitrogen, varying from 0.7 % – 3.0% and 0.3 % – 1.0% respectively. Moreover, a maximum fraction of additive is defined, and type of additive is either restricted to particular raw materials or at least has to be stated according to all standards except DIN 51731.

Table 2: Specification of wood pellet qualities according to ÖNORM EN 14961-2 and previous national standards and quality labels for selected countries [GRIESMAYR 2008].

Country Standard, quality label (class)	EN 14961- 2 A1	EN 14961-2 A2	EN 14961-2 B	Austria ÖNORM M 7135 HP 1	Germany DINplus DIN 51731		Sweden SS 187120 Group	France ITEBE Extra ITEBE Supé- rieure	
Diameter in mm	6 (± 1) or 8 (± 1)	6 (± 1) or 8 (± 1)	6 (± 1) or 8 (± 1)	4 ≤ D and D < 10	4 ≤ D and D < 10	4 ≤ D and D < 10	n.d.	6 ± 1	6 ± 1
Length in mm	≥ 3.15; ≤ 40 ¹⁾	≥ 3.15; ≤ 40 ¹⁾	≥ 3.15; ≤ 40 ¹⁾	≤ 5xD	≤ 5xD	< 50	≤ 4 x D	10 – 30 ⁵⁾	10 – 30 ⁵⁾
Density in kg/dm ³	n.d.	n.d.	n.d.	≥ 1.12	≥ 1.12	1.0 – 1.4	n.d.	> 1.15	> 1.15
Bulk density in kg/m ³	≥ 600	≥ 600	≥ 600	n.d.	n.d.	-	≥ 600	≥ 650	≥ 650
Water content in %	≤ 10	≤ 10	≤ 10	≤ 10	≤ 10	< 12	≤ 10	< 10	< 10
Ash content in %	≤ 0.7	≤ 1.5	≤ 3.0	≤ 0.5	≤ 0.5	< 1.5	≤ 0.7	< 1	< 1.5
Net Calorific Value in MJ/kg	≥ 16.5; ≤ 19	≥ 16.3; ≤ 19	≥ 16.0; ≤ 19	≥ 18	≥ 18	17.5 – 19.5	≥ 16.9	> 16.9	> 16.9
S in %	≤ 0.03	≤ 0.03	≤ 0.04	≤ 0.04	≤ 0.04	≤ 0.08	≤ 0.08	n.d.	n.d.
N in %	≤ 0.3	≤ 0.5	≤ 1	≤ 0.3	≤ 0.3	≤ 0.3	n.d.	≤ 0.3	≤ 0.3
Cl in %	≤ 0.02	≤ 0.02	≤ 0.03	≤ 0.02	≤ 0.02	≤ 0.03	≤ 0.03	< 0.03	< 0.03
Fines in %	≤ 1	≤ 1	≤ 1	n.d. ³⁾	n.d. ³⁾	n.d.	≤ 0.8	n.d.	n.d.
Additives in %	≤ 2 ²⁾	≤ 2 ²⁾	≤ 2 ²⁾	≤ 2	≤ 2	≤ 2	no limit ⁴⁾	≤ 2 ⁶⁾	≤ 2 ⁷⁾
Mechanical durability in %	≥ 97.5	≥ 97.5	≥ 96.5	≥ 97.7	≥ 97.7	n.d.	n.d.	≥ 97.7	≥ 95
n.d. not defined									

¹⁾ Amount of pellets longer than 40 mm can be 1 w-%. Maximum length shall be < 45 mm.

²⁾ Type (e.g. starch, corn flour, potato flour, vegetable oil).

³⁾ Fines have to be removed.

⁴⁾ Fraction and type of additive have to be stated.

⁵⁾ 90 % by weight of the pellets have to be within this range.

⁶⁾ Chemically untreated primary products from agricultural or forestry biomass.

⁷⁾ Type of additive has to be stated.

3.2 Automatically stoked small-scale combustion units

Slag formation in the grate section of biomass combustion units is particularly problematic for automatically stoked appliances, where a trouble-free combustion process is required to ensure continuous operation for a long period of time.

Automatically stoking furnaces are further differentiated considering furnaces with fixed bed combustion, fluidised bed combustion and dust combustion [MARUTZKY 1999]. However, considering the scope of the thesis which is focused on small scale appliances, only fixed bed combustion systems are considered in the following section, focusing on combustion principles as well as grate systems and ash removal solutions.

3.2.1 Combustion principles

The three main combustion principles for small-scale fixed bed combustion are specified according to the way of fuel feeding. The three principles shown in Figure 1 are described below.

Top feed burners

This type of burner has been specially developed and is only applicable for pellet combustion in small-scale appliances. Top-fed pellets fall onto the fire bed, established either on a grate or in a retort, where primary and secondary air are supplied from below or sideways. [KALTSCHMITT 2009] The separation of the feeding system and the fire bed ensures the effective protection against back-burn into the fuel storage. The proper distance between the combustion retort and the feeding system prevents early ignition of pellets in the feeding system [OBERNBERGER 2002]. This feeding system allows very accurate feeding of pellets according to the current heat demand and is thus often used in furnaces with very small nominal heat flows [MUSIL-SCHLÄFFER 2010].

Underfeed burners

In underfeed burners the fuel is fed from below into a retort. A certain amount of air is supplied as primary air into the retort where drying, off-gassing and carbon combustion take place. Volatile gaseous compounds are burnt in an afterburner chamber requiring secondary air supply. Underfeed burners are best suited for low-ash fuels like wood pellets or wood chips. Moreover, fine grained and consistent size of the fuel particles is required to ensure smooth operation of the fuel screw. Underfeed burners are applicable for appliances in the range of 10 kW up to 2.5 MW. [KALTSCHMITT 2009]

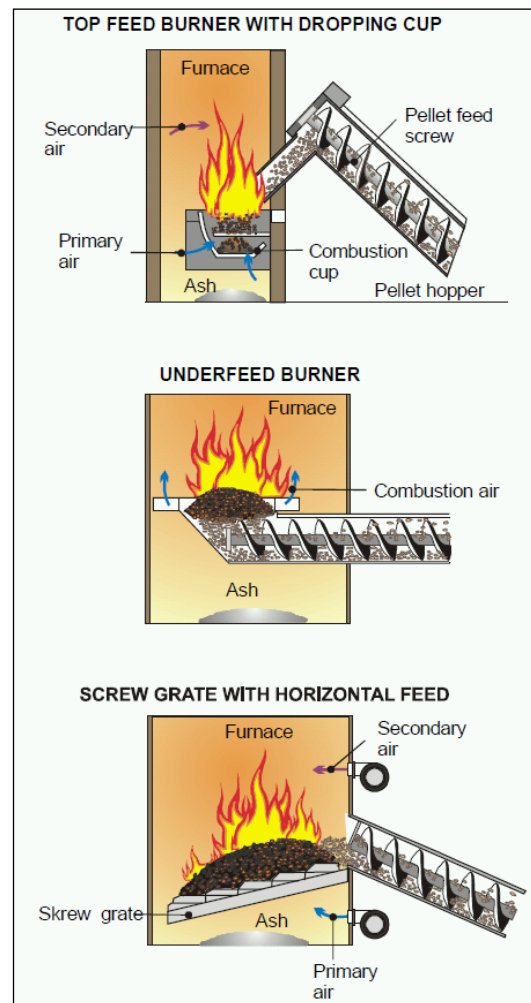


Figure 1: Basic principles of small-scale combustion technologies [ALAKANGAS 2002].

Horizontal feed

In horizontal feed burners the fuel is supplied sideways onto a grate or moving floor system using either a screw for fine grained homogenous fuel particles or a pusher for coarse and heterogeneous material. Primary air is supplied to the fuel bed. Therefore, the grate section is cooled, thus preventing slag formation or overheating of the burner material. Secondary air is supplied above the fuel bed. Units up to a heat output of 100 kW are sometimes only equipped with a fixed grate, whereas larger appliances require moving grates like e.g. pusher-type grate or roller grate, or are designed as moving floor technology. However, these grates can also be applied in a lower power range. Horizontal feed systems with a water cooled retorte are particularly suited for ash-rich fuels with increased slag formation tendency. [HARTMANN 2013]

3.2.2 Grate systems and ash removal solutions

Different grate systems are used dependent on the range of capacity and type of fuel used. Basic principles in this regard are tilting grate, fixed grate (optional with ash scraper), roller grate and reciprocating grate. Moreover, several systems are designed without a grate, and the fire bed is established in a retort, on a (pusher) plate or in a tunnel. [HARTMANN 2009]

The basic principles with and without grate are shown in Figure 2 and Figure 3 respectively, including typical capacity ranges and fuel types applied.

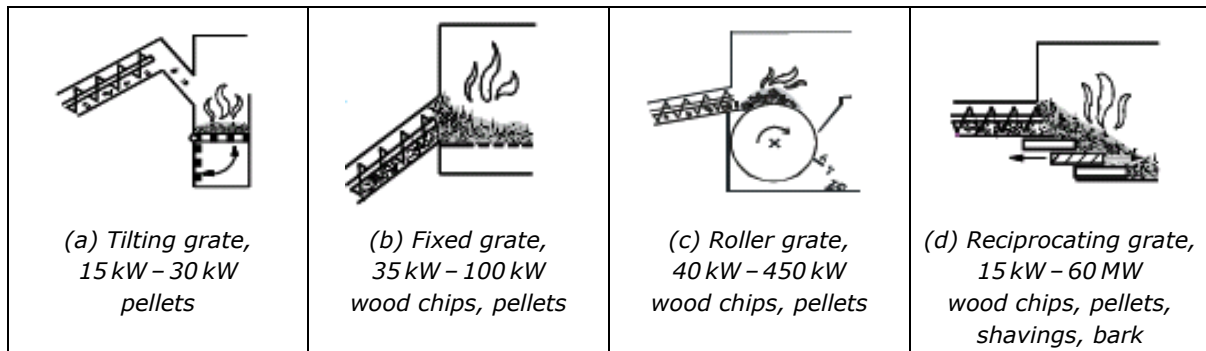


Figure 2: Basic types of grate systems including the typical range of capacity and fuel types applied, adopted from HARTMANN 2007.

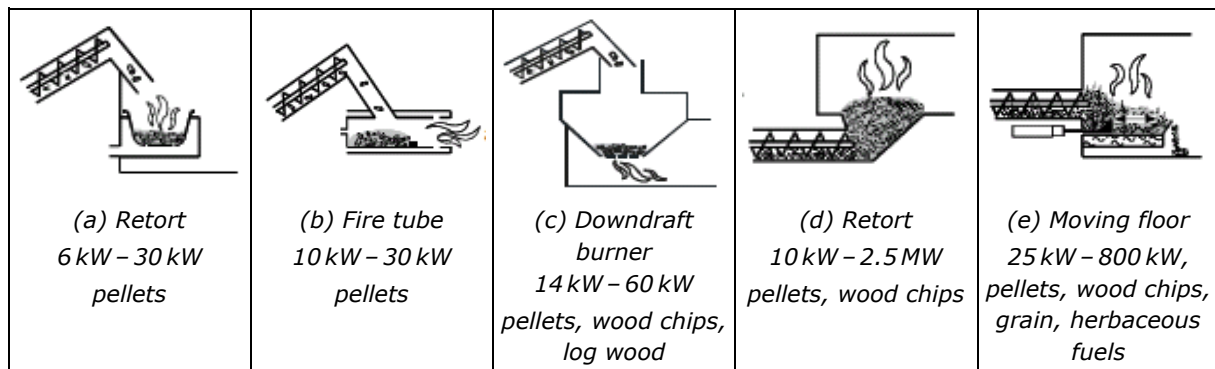


Figure 3: Basic types of burner systems without a grate including the typical range of capacity and fuel types applied, adopted from HARTMANN 2007.

Systems that do not enable continuous ash discharge (cf. Figure 2 (a) and Figure 3 (a) and (b)) are mainly used in small appliances. However, fixed grate systems with horizontal feeding or underfeed burners are used for wood chips and pellets, and are applied in a wide range of capacity. For ash rich fuels with potentially increased slag formation tendency pusher plate systems or reciprocating grates are suggested.

Different variants of the above described principles are available. Moreover, additional systems have been developed for particular fields of application, like e.g. the rotating grate for improved ash and eventual slag discharge by ETA Co. [ETA 2013], the auger-burner principle for a broad variety of biomass fuels by Ligno Co. [BUCHEGGER 2011], the double reciprocating grate by Hargassner Co. (for non-woody biomass fuels) or the innovative rotary-grate combustion system for wood chips or pellets by KWB Co. [KWB 2013]. In Figure 4 drawings of three of these innovative grate systems are shown exemplarily.

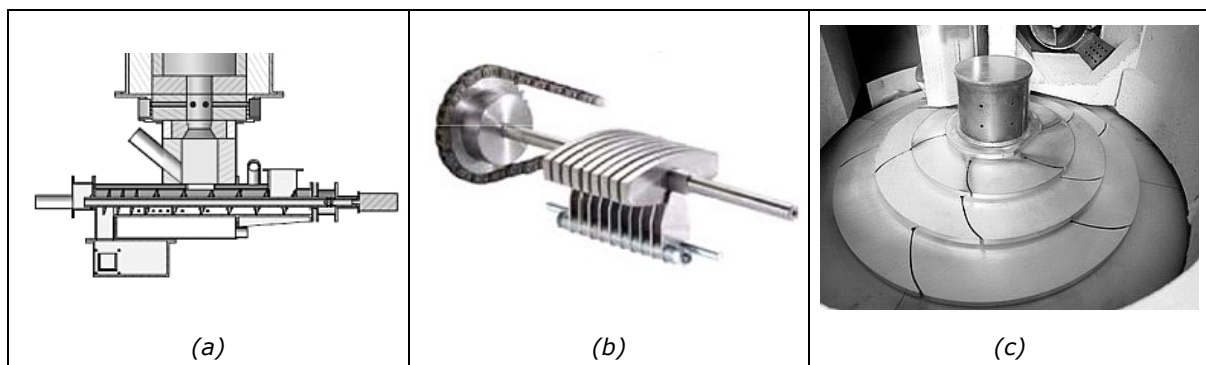


Figure 4: Innovative grate systems; (a) auger burner by Ligno Co. [BUCHEGGER 2011], (b) rotating grate by ETA Co. [ETA 2013] and (c) innovative rotary-grate by KWB Co. [KWB 2013].

3.3 Principles of ash and slag formation from biomass combustion

Ash is a complex mixture of various mainly inorganic compounds, emerging from fuel constituents during the combustion process. The following section provides an overview about ash forming elements and their occurrence in plant material, and also influencing factors on the concentration of particular elements are discussed.

Mechanisms of ash and slag formation in biomass combustion are described, and the main processes and transformations during biomass combustion as well as influencing factors in this regard are surveyed. Also, information on possible ash melting mechanisms is provided. Moreover, ash chemistry is described in terms of elemental composition of ash and slag samples as well as typical compounds in ashes from different biomass fuels.

Available information about the release of inorganic elements is summarised, examining different influencing factors in terms of temperature, fuel composition and combustion conditions. Finally, the properties of different ash fractions from fixed bed biomass combustion are described.

Basic information on measures to influence the ash melting properties of biomass fuels is given, considering raw material selection, pre-treatment and processing as well as the use of additives.

3.3.1 Ash forming elements

Description, occurrence and classification of ash forming elements

About 80 % – 90 % of the plant material are water. The main constituents of dry matter in biomass are cellulose, hemicellulose and lignin. These biopolymers, solely made of carbon (C), hydrogen (H) and oxygen (O), form the matrix of biomass. In addition, biomass contains a number of other elements – often referred to as *ash forming elements*. Compared to the main components C, H and O concentrations of these elements in the plant are much lower, nevertheless they are of significant importance being part of essential compounds or taking part in metabolic reactions. These elements can be classified e.g. based on their concentration in the plant or their physiological function or relevance. Figure 5 gives an overview about elements that are usually found in plants.

Main Elements C, O, H Typical concentration: C, O >40% dm and H~6% dm	Other elements Not definite essential but advantageous: Na, Cl, Si Necessary for some plants: Co, V Not essential, toxic in higher concentrations: J, F, Al, Se, Ni, Pb, Cd and other heavy metals
Macronutrients N, P, S, K, Ca, Mg, Fe ⁺ Typical concentration: mg/g dm	
Micronutrients Fe ⁺ , Mn, Cu, Zn, Mo, B Typical concentration: µg/g dm	

Figure 5: Classification of elements according to their role and concentration in biomass (adapted from Mengel 1991)

Apart from water, C and O form the main components of the plant structure, amounting to more than 40 % of dry matter each. Nutrients are essential for plant growth and play a major role e.g. for water regulation or in metabolic reactions. Macronutrients are needed in larger amounts, whereas micronutrients are also essential, but required in smaller quantities. It is not proven if Na, Cl and Si are essential, but for most plants a positive effect can be observed; some elements like Co or V are only needed by particular plants. Moreover, elements without advantageous effects or even elements with toxic impact might be absorbed. [MENGEL 1991]

Table 3 provides an overview about the role and occurrence of relevant plant nutrients. Apart from plant-specific elements, there can also be a significant amount of mineral matter in biomass raw materials, originating from impurities like e.g. soil or sand due to harvesting, handling or processing.

According to solid biofuels-standards, elements are classified regarding their occurrence in biomass fuel ashes. In this regard Al, Ca, Fe, Mg, P, K, Si, Na and Ti are considered as major elements, and As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, V and Zn as minor elements [ÖNORM CEN/TS 15290, ÖNORM CEN/TS 15297].

Table 3: Function and occurrence of relevant plant nutrients [MENGEL 1991]

Element		Role/function in plant	Occurrence in plant
Nonmetal	C	Basic components of organic molecules, formation of supporting tissue	Organic molecules (mainly cellulose, lignin and pectine)
	H		
	O		
	N	N, S, P are essential for the formation of proteins, nucleic acids, coenzymes and prosthetic groups, and therefore of significance for plant metabolism	Nitrates, amino acids, acid amides
	S		Various organic sulphur compounds, sulfates
	P		Inorganic phosphate, organic phosphate (ADP, ATP, part of nucleic acids and phospholipids)
	B	Structure of the cell wall, impact on enzyme activity and mass transfer across membranes, essential for the synthesis of nucleic acids and thus the formation of proteins	Borates with plant related alcoholic groups, B(OH) ₃ associated in a complex with diols
	(Si)	Increases the stability of the cell wall (reduction of transpiration and fungal attack)	Ester-type bonds or as SiO ₂ deposits
alkali metal	K (Na)	Osmotic effect and electric balancing of anions, conformation of enzymes	free cation
alkali earth metal	Mg	Link for reactants, influence on the permeability and potential of membranes, influence on enzymes, takes part in hormone reactions	salts (Mg-oxalate, phytin), ionic (free or sorptiv gebunden), part of chelate (e.g. chlorophyll = 15 % – 20 % of total magnesium)
	Ca		ionic, considerable amounts adsorbed to indiffusible anions

Table 3 (continuation): Function and occurrence of relevant plant nutrients [MENGEL 1991]

Element		Role/function in plant	Occurrence in plant
Heavy metal	Fe	Catalytic effect as part of prosthetic groups	Fe(III)-dicitrat, ferritin, haem or hemin (prosthetic group)
	Mn	Activation of enzymes (similar to Mg^{2+}), role in photosynthesis reaction	Mn^{2+} mainly coordinated in complexes
	Cu	Transport of electrons (e.g. in photosynthesis reactions, catalytic effect in redox reactions)	Cu-proteins (Cu(I) or Cu(II) in complex with aminoacids
	Zn	Activation of various enzymes	Zn^{2+} or organically bound as Zn-complex
	Mo	Essential component in oxidoreductases	Mo(VI) organic complexes (enzymes)
	(Cl)	Effect on osmotic potential, electric potential and conductivity	Cl^-

Influencing factors on the elemental composition

The elemental composition of biomass raw materials and the concentration of particular elements respectively is influenced by various factors.

In general, major differences are found between perennial and annual biomass, where variations are much stronger due to an increased metabolic activity. Furthermore, plant genus and species determine the elemental composition: For wood e.g., a correlation of the concentration of ash forming elements and type of wood can be observed: A general trend for the total amount of ash forming elements in the plant of pine < spruce < oak < beech was found by RADEMACHER 2005. Also, differences regarding the amount of ash forming elements, and in particular N and Cl among different genotypes of Miscanthus were determined e.g. by LEWANDOWSKI 2003 and CLIFTON-BROWN 2002. Moreover, variations regarding the elemental composition of Miscanthus dependent on the stand age were observed, in particular between first year and older crops, because of the physiological changes that occur with plant age [CLIFTON-BROWN 2002].

The soil quality also has a major influence: In general, higher concentrations of nutrients and harmful elements in the soil lead to an increased uptake in the plants, also depending on gradients in the soil and the rooting depth. Besides the chemical composition also geological properties and the pH-value of the soil impact the absorption of particular elements [MENGEL 1991]. In this regard also fertilising is an important factor. Moreover, depositions or absorption from atmosphere might be relevant.

Apart from plant innate factors, harvesting time may be an important factor: Delayed harvest of Miscanthus e.g. in general results in a reduction of ash content as well as concentrations of potassium (K), chloride (Cl) and nitrogen (N) [LEWANDOWSKI 2003, CLIFTON-BROWN 2002]. Furthermore, major differences with regard to elemental composition can be found for different parts of a plant: Regarding wood e.g., ash forming elements are preferably bound in bark and needles or leaves, where also the strongest variations can be observed due to increased availability of particular elements (e.g. after fertilisation) [RADEMACHER 2005]. Therefore, processing of the raw material and selection of a particular raw material fraction is crucial with regard to chemical composition.

All above mentioned parameters influence the physical and chemical properties of a biomass raw material, and a precise prediction of the plant composition is impossible, due to complex interactions. Therefore, properties of raw materials from different sources and parts of the plant can only be evaluated by estimating the impact of several factors based on previous experiences.

3.3.2 Mechanisms of ash and slag formation in biomass combustion

During the combustion process, organic compounds undergo pyrolytic decomposition, followed by combustion of the resulting gaseous and solid products. Residual ash is formed from both inorganic compounds of the plant and mineral impurities like e.g. soil in the raw material.

Processes and transformations during biomass combustion

Numerous physico-chemical transformations of organic and inorganic matter take place during biomass combustion. General processes in this regard are described by VASSILEV 2014, and are summarised in Table 4.

Table 4: General processes of physico-chemical transformations observed in biomass ashes by VASSILEV 2014.

Temperature range	Process
200 °C – 850 °C	Combustion of organic matter
~ 500 °C	Fragmentation (disintegration) of particles
700 °C – 900 °C	Initial
700 °C – 1100 °C	Extensive
700 °C – 1300 °C	Significant
	} agglomeration or occasionally swelling of particles
~ 700 °C	Initial
900 °C – 1100 °C	Extensive
1100 °C – 1500 °C	Complete
	} fusion of particles or minerals with different melting points
500 °C – 1500 °C	Various new phase crystallizations
700 °C – 1500 °C	Melt/glass formation

According to Vassilev 2014 the following transformations take place during the biomass combustion process:

- Transformation of original organic and inorganic matter (already initial to devolatilisation of organic matter and burning of combustible gases and char), with the formation of intermediate and less stable organic and inorganic compounds
- Subsequent formation of more stable silicates, phosphates and oxides
- Melting accompanied by dissolution of the refractory minerals with increasing combustion temperatures

- Crystallization of melt and formation of glass accompanied by some salt condensation and hydroxylation, hydration and carbonation of newly formed phases during cooling of biomass ash
- Post-combustion transformations of the newly formed minerals and phases to stable species

These results are in good accordance with reactions observed e.g. by OLANDERS 1995, supposing Mg to transform from biologically associated Mg via an amorphous intermediate to magnesium oxide, which is only found at temperatures of 700 °C and above [OLANDERS 1995]. Moreover, a primary association of alkali and alkaline earth metals with sulphate, carbonate and chloride ions is observed [OLANDERS 1995].

Ash transformation chemistry

Biomass ashes show a broad variety with regard to elemental composition, and numerous compounds could be formed from the available elements. In order to determine the most probable reaction pathways, a simplified conceptual model was formulated by BOSTRÖM 2012, summarising and formalising empirical biomass ash transformation phenomena and observations. Taking a starting point at the concentrations of the main ash-forming elements, fundamental chemical thermodynamics, and basic inorganic high-temperature chemical concepts are applied. Moreover, a hypothetical division of ash transformation into primary and secondary reactions is used in order to organize the properties of the ash-forming elements into a conceptual model. [BOSTRÖM 2012].

- Primary reactions are mainly used to denote and define the mutual affinity of the ash-forming elements to oxygen in relation to the oxygen affinity of the carbon-hydrogen matrix of the fuel, thus isolated from any further reaction. Some vital information about thermal stability, e.g., refractivity and/or volatility, of the primary or initial products is also gained from this approach.
- Secondary reactions describe the essential ash-forming process considering the compounds resulting from primary reactions and their particular properties. Therefore, these compounds are divided into two categories, basic and acidic compounds, and are roughly arranged according to their reactivity in a simplified approach.

Even though this concept is a simplification (e.g. disregarding the formation of mixed compounds like e.g. Ca-K-phosphates), it provides basic information about preferred reactions in ashes with particular compositions. In Table 5 primary products of ash-forming elements according to this concept are presented.

Table 5: Primary products of ash-forming elements from the initial stages of combustion (divided into basic and acidic compounds and arranged according to reactivity) according to BOSTRÖM 2012.

	Basic compounds	Acidic compounds
Reactivity + ↑ -	KOH(l,g) (K ₂ O)	P ₂ O ₅ (g)
	NaOH(l,g) (Na ₂ O)	SO ₂ (g)/SO ₃ (g)
	CaO(s)	SiO ₂ (s)
	MgO(s)	HCl(g) (Cl ₂)
	H ₂ O(g)	CO ₂ (g)
		H ₂ O(g)

Major conclusions regarding the ash transformation chemistry according to BOSTRÖM 2012 are:

- The formation of phosphates compared to silicates is preferred (cf. LINDSTRÖM 2007)
- The formation of silicates is favored compared to carbonates or oxides. Therefore, these compounds are only formed with a surplus of basic compounds.
- In Ca-rich ashes, a high fraction of P remains in the bottom ash forming phosphates.
- A surplus of Ca/Mg may cause a depletion of K in silicate melts due to higher stability of this compounds, where K is replaced by Ca/Mg in silicate compounds
- Increased amounts of Al can increase the melting temperatures due to the formation of K-Al-silicates

Investigations of different authors confirm these findings: Analysing ashes from bark/wood chips and straw, Ca was found to be more stable in silicate compounds than oxides at combustion temperatures by OLANDERS 1995. Increased formation of phosphates compared to silicates was found in a reed canary grass sample by GILBE 2008 (1). No carbonates or oxides were formed from alkaline earth metals in ashes from various cereals also showing considerable amounts of Si and P [LINDSTRÖM 2007], and in ashes from woody biomass, a considerable fraction of silicates of alkaline earth metals was formed compared to carbonate compounds [LINDSTRÖM 2008]. In Table 6 main and minor crystalline compounds in both bottom ash and slag samples from different types of biomass and combustion units.

Table 6: Typical compounds in ash and slag samples from the combustion of different biomass fuels, summarised from OLANDERS 1995, GILBE 2008 (1) and LINDSTRÖM 2007.

Fuel	Crystalline compounds in bottom ash		Crystalline compounds in slag	
	Main	Minor	Main	Minor
Saw dust ^a	CaO, CaCO ₃ , K ₂ Ca(CO ₃) ₂	Ca(OH) ₂	No slag	No slag
Bark/wood chips (50:50) ^b	CaO, SiO ₂ , MgO	CaCO ₃ , KAlSi ₃ O ₈ , Ca ₂ SiO ₄ , Ca ₂ MgSi ₂ O ₇ , Ca ₃ Mg(SiO ₄) ₂ , Fe ₂ O ₃	Not available	Not available
Bark/wood chips (60:40) ^b	CaO, SiO ₂ , MgO	CaCO ₃ , KAlSi ₃ O ₈ , Ca ₂ SiO ₄ , Ca ₂ MgSi ₂ O ₇ , K ₂ CaSiO ₄	Not available	Not available

Table 6 (continuation): Typical compounds in ash and slag samples from the combustion of different biomass fuels, summarised from OLANDERS 1995, GILBE 2008 (1) and LINDSTRÖM 2007.

Fuel	Crystalline compounds in bottom ash		Crystalline compounds in slag	
	Main	Minor	Main	Minor
Bark spruce ^a	CaO, Ca ₃ Mg(SiO ₄) ₂	CaCO ₃ , K ₂ SO ₄ , MgO Ca(OH) ₂ , SiO ₂	Ca ₂ Mg(Si ₂ O ₇), CaSiO ₃ , Ca ₂ SiO ₄	No more than main compounds
Salix ^a	CaO, CaCO ₃	Ca ₂ SiO ₄ , MgO, Ca(OH) ₂ , K ₂ Ca(CO ₃) ₂ + sand minerals	Ca ₂ Mg(Si ₂ O ₇)	Ca ₃ Mg(SiO ₄) ₂ , KAlSiO ₄ , KAlSi ₂ O ₆ , CaSiO ₃ , SiO ₂
Straw ^b	SiO ₂ , K ₂ SO ₄ , KCl	KAlSi ₃ O ₈ , Ca ₂ SiO ₄ , Ca ₂ MgSi ₂ O ₇ , Ca ₃ Si ₂ O ₇	Not available	Not available
Reed canary grass (la) ^a	Ca ₉ MgK(PO ₄) ₇	SiO ₂ (quartz, cristobalite), K ₂ SO ₄	Ca ₉ MgK(PO ₄) ₇	SiO ₂
Oats ^c	SiO ₂ , MgKPO ₄	CaK ₂ P ₂ O ₇ , KH ₂ PO ₄ , MgK ₂ SiO ₄ , KCl	SiO ₂ , MgKPO ₄	CaK ₂ P ₂ O ₇
Barley ^c	SiO ₂ , MgKPO ₄ , CaK ₂ P ₂ O ₇	KPO ₃ , KH ₂ PO ₄ , CaKPO ₄ , KCl, K ₂ SO ₄	SiO ₂ , MgKPO ₄ , CaK ₂ P ₂ O ₇	MgK ₂ SiO ₄
Rye ^c	MgKPO ₄ , CaK ₂ P ₂ O ₇	KPO ₃ , KH ₂ PO ₄ , Ca ₁₀ K(PO ₄) ₇ , MgK ₂ P ₂ O ₇ , MgO	MgKPO ₄ , CaK ₂ P ₂ O ₇ , MgK ₂ P ₂ O ₇	Ca ₁₀ K(PO ₄) ₇ ,
Wheat ^c	MgKPO ₄	KPO ₃ , KH ₂ PO ₄ , CaK ₂ P ₂ O ₇ , Ca ₁₀ K(PO ₄) ₇ , MgK ₂ P ₂ O ₇ , MgO	MgKPO ₄ , CaK ₂ P ₂ O ₇	Ca ₁₀ K(PO ₄) ₇ , MgK ₂ P ₂ O ₇

^a GILBE 2008 (1)

^b OLANDERS 1995

^c LINDSTRÖM 2007

Ash fusion mechanism

Two basic mechanisms of melt formation that were found for coal ashes are presented by VASSILEV 2014, notably

- Melting-dissolution described as the formation of initial and active low-temperature melts with low viscosity (high mobility) that quickly dissolve the residual refractory minerals or phases in the system, and
- Softening-melting described as prolonged softening and subsequent melting of solid phases and formation of less active and high-temperature melts with high viscosity (low mobility) that result in sluggish flow and depressed dissolution of the residual refractory constituents in the system.

Even though these mechanisms are valid for silicate systems like coal ashes and biomass ashes with more acid tendencies, it is concluded that in general they can be applied to biomass ashes as well, and that the mechanism "melting-dissolution" is more typical for biomass ashes compared to coal ashes that exhibit the more characteristic "softening-melting" mechanism. [VASSILEV 2014] However, additional ash fusion mechanisms and sub-mechanisms related to biomass ashes can also occur, due to the much more variable composition of biomass compared to coal. [VASSILEV 2014]

The “melting-dissolution”-mechanism as described by Vassilev 2014 is in good accordance with the slag formation mechanism suggested e.g. by GILBE 2008 (1) or BOSTRÖM 2012 where the melting process is initiated by a sticky K-Si-melt for Si-dominated ashes or K-phosphates for P-dominated ashes, subsequently dissolving refractory compounds.

However, several compounds that can be the major reasons for the initial liquid formation with increasing temperatures are compiled by VASSILEV 2014 including K- and Na-nitrates and hydroxides, K-Na silicate eutectics, Fe and Mn chlorides, K- and Na-chlorides and carbonates, Na-sulphate, K-sulphate, Mg-sulphate, acid plagioclases, feldspar, illite and montmorillonite, Ca-sulphate and basic plagioclases, and Ca- and Mg- silicates and oxides, kaolinite, and silicate minerals.

Elemental composition of ash and slag samples

The above described melting mechanism may cause differences with regard to elemental composition of ash and slag samples, due to initial melt formation of particular compounds: Significantly increased fractions of Si and Al in slag samples of woody biomass (sawdust, logging residues and bark) were found by ÖHMAN 2004 (1). Also increased amounts of Si in slag samples from the combustion of bark was found by LINDSTRÖM 2008, whereas slag from the combustion of forest residues showed increased concentrations of Ca. Analysing the combustion residues of different cereals, increased amounts of Si in the slag of barley and increased values of P in the respective slag samples of barley, rye and wheat were determined. Moreover, an increased concentration of K in the slag of wheat compared to the respective ash sample was found. [LINDSTRÖM 2007]

Increased concentrations of Si and/or Ca in the slag of particular samples were also observed by GILBE 2008 (2).

However, among the variety of fuel samples both considerable and minor differences are found regarding the composition of bottom ash and the respective slag, and no general tendency was identified in this regard.

Additional influencing factors

Vassilev concludes that despite identical chemical composition different behavior due to diverse mineral composition can be observed, and even samples with similar or identical mineral composition may exhibit different ash fusion characteristics due to

- Size and morphology of the minerals
- Association of the minerals in aggregates, particles and agglomerates
- Isomorphic substitution and other element impurities in the minerals
- Sample preparation, heating rate, atmosphere

[VASSILEV 1995]

However, apart from fuel- and ash composition, there are a number of additional factors like prevailing temperature, residence time or surrounding atmosphere influencing the ash transformation process and consequently determining the compounds formed from the available elements and thus the properties of the resulting ash.

3.3.3 Release of ash forming elements

Basic processes and transformations during biomass combustion have been described in the previous chapter. From the variety of transformation reactions also a number of volatile compounds may be formed and released from the bottom ash. A basic knowledge of typical release rates of inorganic elements as well as an understanding of basic mechanisms and the most relevant influencing factors in this regard are essential for an adequate evaluation and interpretation of experimental results (e.g. ash- and slag-analyses).

The release of inorganic elements from the fuel has frequently been investigated focusing on problems such as slagging and fouling, corrosion and the formation of harmful emissions of gases and particulate matter [e.g. VAN LITH 2006, LLORENTE 2006, FRANDSEN 2005, FRANDSEN 2007, KNUDSEN 2004, VAN LITH 2008, LANG 2006, THY 2000, THY 2006 (1)]. Therefore, in particular the release of S and Cl, the alkaline metals K and Na and also heavy metals like Pb or Zn are considered, and the influence of temperature level or type of fuel and fuel composition respectively are studied. In this regard both woody as well as annual biomass have been taken into account.

However, available data mainly originate from laboratory- or lab-scale reactor tests, conducted under well controlled conditions, and sometimes even pre-processed laboratory ash is used. Using small fuel samples, as it is done in laboratory tests, mainly the primary release is investigated, whereas secondary reactions might not be considered (cf. VAN LITH 2006). Moreover, these tests are usually conducted under batch-operation, and fuels are exposed to the experimental conditions for a very long period of time – some hours in many cases – thereby not representing combustion conditions in real fixed bed combustion appliances. Hardly any results from stationary combustion experiments are available, and the influence of combustion conditions in terms of e.g. residence time or air supply has not been investigated. Only a few experiments have been conducted under real application conditions in commercial combustion units (e.g. a 20 kW pellet boiler [GILBE 2008 (1)] or a 440 kW pilot-scale boiler [FRANDSEN 2007]).

In Figure 6 release data for Cl, K, S and Zn gathered from literature are presented.

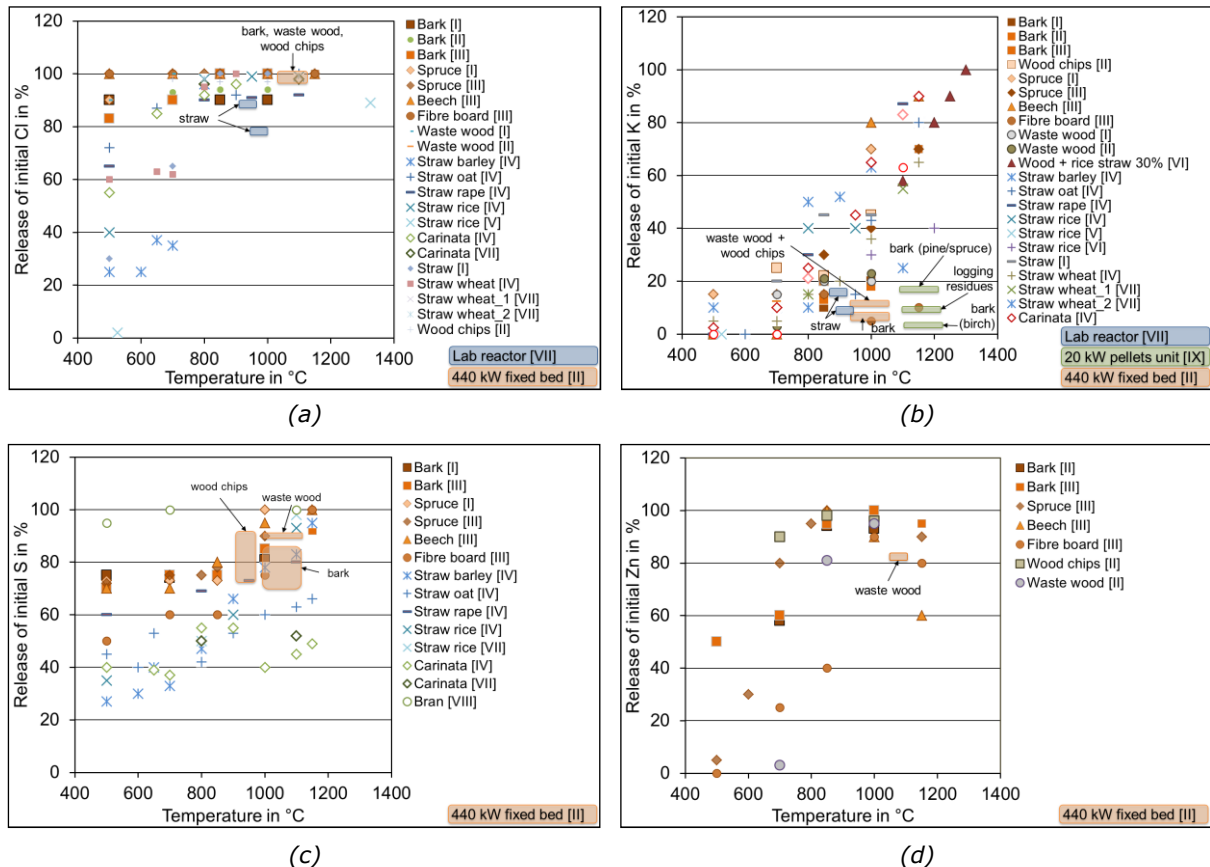


Figure 6: Summary of release data gathered from literature for chlorine (a), potassium (b), sulphur (c) and zinc (d) at different temperatures. References: [I]...FRANDSEN 2005, [II]...FRANDSEN 2007, [III]...VAN LITH 2008, [IV]...KNUDSEN 2004, [V]...THY 2006 (1), [VI]...THY 2006 (2), [VII]...LANG 2006, [VIII]...WU 2011, [IX]...GILBE 2008 (1)

Influence of temperature on elemental release

The influence of temperature on the elemental release is investigated in numerous studies [FRANDSEN 2005, FRANDSEN 2007, VAN LITH 2008, THY 2006 (1), THY 2006 (2), KNUDSEN 2004, LANG 2006, WU 2011], and considerable influence in this regard was found for potassium (K), sodium (Na), chlorine (Cl), sulphur (S), phosphorous (P), lead (Pb) and zinc (Zn).

Laboratory experiments showed that the **release of potassium** is highly dependent on temperature. An average loss of 0 % – 20 % was found up to 500 °C, increasing significantly with higher temperatures above 700 °C. For temperatures around 1100 °C about 60 % – 90 % of the potassium in the fuel were released [LLORENTE 2006, FRANDSEN 2005, KNUDSEN 2004, VAN LITH 2008, WU 2011, LANG 2006].

Considerable differences between ashes from laboratory tests and real combustion appliances were found in this regard. E.g. relatively low release values of maximum 20 % were found when firing different types of pellets (straw, wood, reed canary grass, hemp) in a commercial pellet boiler, even though temperatures were assumed to be around 1200 °C [GILBE 2008 (1)]. This could be explained by different combustion conditions in real appliances like e.g. fast heating and off-gassing, shorter residence time or locally differing temperatures maybe providing for different ash transformation reactions. Moreover, conditions for the mass

transfer are different for dense pellets compared to small amounts of fine ground material. However, no previous work has been found in this regard.

The release of **sodium**, which is very similar to potassium with regard to its chemical properties, was also found to be temperature dependent. For 700 °C about 10 % – 20 % were found to be released, at a temperature of 800 °C about 50 % release were found, and above 1000 °C a release of 60 % – 70 % was determined [VAN LITH 2006].

Considerable variations were observed for the release of **chlorine** from the fuel below 700 °C – 800 °C in laboratory tests, varying between 20 % and 80 % depending on type and composition of the fuel. Above these temperatures, a release of 90 % – 100 % has been reported for any type of biomass. In line with these findings, about 100 % of the initial chlorine were found to be released during combustion tests in a 440 kW boiler with different woody biomass fuels [FRANDSEN 2007], whereas residual fractions of 12 % and 23 % respectively were found in ashes from the combustion of wheat straw in a lab-scale combustion unit [LANG 2006].

Strong variations were observed for the release of **sulphur** dependent on the type of fuel: For wood-type fuels, 70 % – 80 % of the initial fuel sulphur are released up to about 800 °C, increasing with higher temperatures to 75 % – 100 % around 1000 °C and 90 % – 100 % at 1200 °C. Lower values were found for different straw fuels, starting with 30 % – 50 % at 500 °C with continuously increasing release rates. A considerable increase was found above 800 °C, and release fractions with 80 % – 100 % were determined at 1000 °C – 1200 °C. However, significantly lower values were found for oat straw and carinata with release fractions of 60 % and 40 % – 50 % respectively. Exceptionally high sulphur release was observed for bran [WU 2011] with 90 % – 100 % over the whole range of 500 °C – 1100 °C. Data from real combustion application are only available for woody biomass fuels, and are in line with results from laboratory tests.

Regarding the release of **phosphorous**, no major changes were found in laboratory ashes produced at temperatures between 400 °C and 800 °C from different types of non-woody biomass (i.e. pine chips, thistle, straw, poplar chips) [LLORENTE 2006]. Also, no major phosphorous-release was determined for 500 °C – 800 °C in laboratory tests with ashes of bran, brassica carinata, rice straw and different wheat straw samples [WU 2011, LANG 2006]. However, at 1100 °C, 3 %, 15 % and 7 % – 29 % of phosphorous were released from ashes of carinata, rice straw and wheat straw respectively [LANG 2006], and about 66 % of the initial phosphorous were released from bran [WU 2011].

A very similar behaviour was observed for the release of **zinc** and **lead** [VAN LITH 2008]. The release of both metals varies a lot in the range of 700 °C – 800 °C, and shows a clear increase with increasing temperature. From 850 °C about 90 % – 100 % of zinc and lead respectively have found to be released for all fuels [FRANDSEN 2007, VAN LITH 2008].

Influence of the fuel composition on the elemental release

Investigations have been conducted showing the influence of elemental concentrations of Ca, Si, K and Na in the ash on the release of sulphur [NORDIN 1995, KNUDSEN 2004], and also the effect of Ca-containing additives was studied in this regard [Lang 2006]. The release of

particular elements dependent on the ash composition has been investigated in experiments with different mixtures of ash samples [Thy 2006_2], and particularly the release of alkaline metals dependent on the chemical composition of the fuel has been investigated by several authors [THY 2000, THY 2006 (2), GILBE 2008 (1)].

Considerable variations regarding the release of **potassium** were observed for different types of fuels [FRANDSEN 2007, Gilbe 2008 (1)]. The release of potassium from straw ashes was found to be low when compared to wood ash [THY 2006 (1)]. Moreover, systematic investigations with rice straw and wood ash blends showed an increasing potassium retention for a higher share of rice straw ash [THY 2006 (2)], which was correlated to the content of Si. Similar results were found correlating potassium retention to a factor calculated from elemental concentrations ($\text{Si}/(\text{Ca}+\text{Mg}+\text{Cl})$), resulting in an increasing retention with increasing factor [GILBE 2008 (1)]. A K-release of about 20 % was observed for straw ashes at a temperature of about 900 °C [KNUDSEN 2004], whereas hardly any K-release from bran-ash at 900 °C was found, which is attributed to low Cl-concentrations, obviating the release of KCl [WU 2011]. With addition of Ca-containing additives, an increased release of K is observed, whereas Al-addition can reduce the release of K from 60 % to 20 % for the same raw material [WU 2011].

For the release of **chlorine**, variations among values gathered from literature can be observed below 700 °C–800 °C, but no clear correlation to the elemental composition is found.

According to BOSTRÖM 2009 and BÄFVER 2009, the release of phosphorous is reduced by adding Ca-containing additives. However, no significant effect of the addition of Ca-containing additives on the release of **phosphorous** was found in laboratory tests [WU 2011], whereas a considerable increase of the K/P-ratio in fly ashes from real combustion appliances on Ca-addition to the fuel was observed [WU 2011].

Data from literature summarised in Figure 6 show increased values regarding the release of **sulphur** from ashes of wood-type biomass compared to straw. A relation of S-release to the Ca/S-relation in the fuel at lower temperatures was found by NORDIN 1995, showing a minor release for fuels with a high Ca/S-relation, whereas above 800 °C, a highly increasing release for all compositions could be observed [NORDIN 1995]. KNUDSEN 2004 showed that the presence of Si can lower the stability of sulphur containing inorganic compounds by reacting with K and Ca, leading to an increased S-release at lower temperatures. In addition to elemental composition, the association and type of bonding of sulphur is considered as relevant with regard to elemental release [WU 2011].

The proportion of **zinc** released from the fuel during thermochemical conversion varies for different types of biomass. No clear correlation with elemental composition could be found, and it is assumed that the degree of retention in the fuel ash or slag is due to the type and nature of the respective chemical bonding [VAN LITH 2008].

Influence of the combustion conditions on the elemental release

Only little work has been done according to the influence of different combustion conditions. Therefore, most conclusions are drawn by comparing results from lab-scale and pilot-scale

tests. Moreover, experiments using different combustion procedures with regard to sample size and air supply have been taken into account [VAN LITH 2006].

The release of **potassium** from biomass pellets during combustion determined by GILBE 2008 (1) was found to be relatively low compared to release rates from different laboratory tests, showing values of around 5 % for Si-rich fuels and about 20 % for Si-lean fuels, although temperatures in the fuel bed were estimated to be around 1200 °C [GILBE 2008 (1)]. These comparable low values might be explained with a short residence time of the fuel ashes in the boiler compared to the exposure time of the samples in the laboratory experiments, and maybe not the whole amount of fuel ash had been exposed to maximum temperatures. Moreover, the mass transfer between fuel and oxidising agent is assumed to be slower due to the size and density of the pellets compared to ground material in the laboratory experiments, resulting in a smaller contact surface, whereby also secondary reactions of intermediate products might be possible. Also, considerable depletion of K from wood ash melt with increasing residence time was found by THY 2000, whereas almost constant values were observed for straw ash melt, which is attributed to the chemical structure of the melt.

Slightly lower fractions of **chlorine** were found to be released from the combustion of wheat straw samples in a laboratory reactor [LANG 2006] when compared to release rates determined for different wood and straw samples in laboratory tests [KNUDSEN 2004, FRANDSEN 2005]. However, results from the combustion of woody biomass fuels in a commercial combustion appliance showed a release of more than 90 % for all investigated samples [FRANDSEN 2007]. Laboratory experiments investigating the release of elements from molten ashes show, that the amount of chlorine is decreasing to low concentrations very quickly when heated up [THY 2000].

A more distinct effect of Ca-containing additives on the release of **phosphorous** from P-rich fuels was observed under real combustion conditions compared to laboratory tests [WU 2011]. A relatively long residence time is supposed to promote the reaction between the Ca-additive and phosphates. Moreover, the height of the fuel/ash bed, which is thicker in the grate-fired plant than in the laboratory-scale experiment, is considered to provide favourable conditions for the reaction between gaseous phosphates and the Ca-additive [WU 2011]. Slight depletion of P from wood ash melt with increasing residence time was found by THY 2000, however, no kinetic factors could be evaluated due to the varying depletion rate with time.

Laboratory experiments showed considerable differences with regard to the release of **sulphur** up to 850 °C under different combustion procedures. It is assumed that the increased residence time and fuel-product-contact in a pile of fuel or charcoal enable secondary reactions resulting in capture of primarily released sulphur containing products. At higher temperatures above 850 °C a rapid increase of sulphur release up to 100 % was observed independent on the combustion conditions. [VAN LITH 2006]

The release of zinc was found to be influenced by the oxidation potential of the gaseous atmosphere. In this regard, the release of zinc is increased under reducing conditions – especially at higher temperature levels. [VAN LITH 2006, ELLED 2008]

3.3.4 Ash fractions from fixed bed biomass combustion

Due to elemental release and particle entrainment by combustion air and flue gas, ash composition varies dependent on the location where it accumulates.

In fixed bed combustion, the main fraction of ash remains as bottom ash in the grate area of the combustion unit. Smaller particles are transported by the flue gas and are separated in the rear part of the boiler, in areas of slow gas velocities or flow reversal. Moreover, finest particles and aerosols occur during biomass combustion. In Figure 7 possible reactions for the formation of aerosols are shown. Coarse fly-ash particles are formed by ash that is entrained from the fuel bed – usually coalesced with condensed alkali and heavy metal compounds, originating from elemental release to the gas phase. Nucleation of alkali compounds, their condensation on CaO nuclei and subsequent agglomeration on the other hand can lead to the formation of aerosols. Moreover, both aerosols and coarse fly-ash particles can also be formed solely by condensation of alkali and heavy metal compounds.

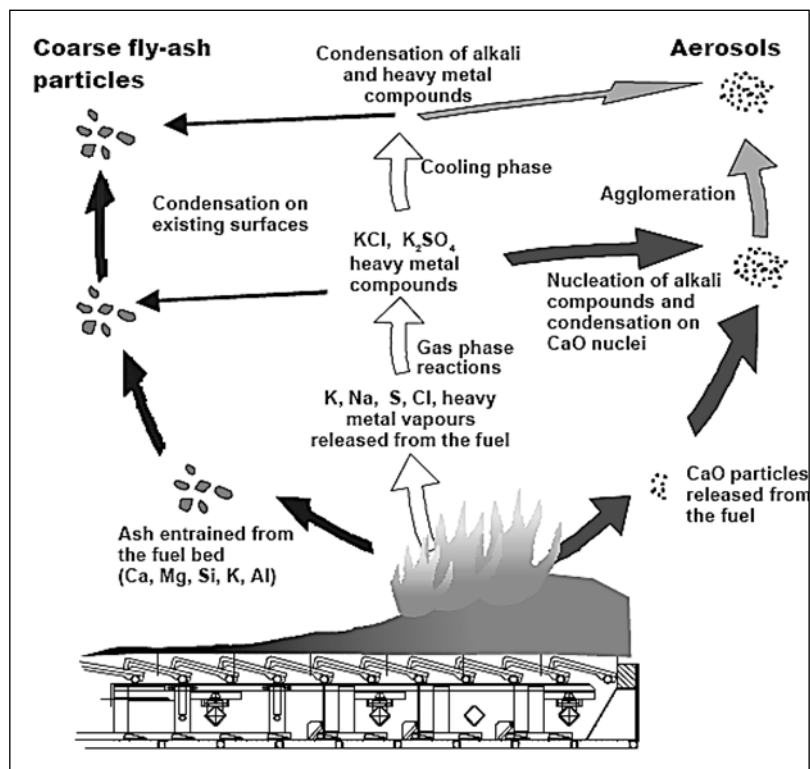


Figure 7: Aerosol formation during fixed-bed combustion of bark [OBERNBERGER 2001 (2)]

In order to remove these particles from the flue gas, additional cleaning facilities like e.g. condensate separator, baghouse filter or electrostatic precipitators are required. However, small appliances are generally not equipped with such device.

In small-scale fixed bed combustion, usually 84 % – 98 % of the ash remain as bottom ash in the grate section, whereas 2 % – 16 % are separated in the heat-exchanger section of the unit. The distribution of ash in particular depends on various factors like ash content of the fuel, size of the fuel particles, geometry of the combustion chamber, combustion technology, air supply and separation technology. The composition of the resulting ash fractions varies

dependent on the ash reactions and separation mechanisms. Usually the fraction of heavy metals and alkali metals increases from bottom ash to cyclone ash and filter ash, whereas the size of the ash particles decreases. Table 7 shows exemplarily the average composition of bottom ash, cyclone ash and the finest ash fraction from the combustion of woody material (bark, wood chips and saw shavings) and straw. [OBERNBERGER 2001 (1)]

Table 7: Average composition of bottom ash, cyclone ash and the finest ash fraction from the combustion of woody material (bark, wood chips and saw shavings) and straw (adapted from [OBERNBERGER 2001 (1)])

	Wood			Straw		
	Bottom ash	Cyclone ash	Fly ash	Bottom ash	Cyclone ash	Fly ash
Nutrients (presented as oxides) in w% dm						
CaO	41.7	35.2	32.2	7.8	5.9	1.2
MgO	6.0	4.4	3.6	4.3	3.4	0.7
K ₂ O	6.4	6.8	14.3	14.3	11.6	48.0
P ₂ O ₅	2.6	2.5	2.8	2.2	1.9	1.1
Na ₂ O	0.7	0.6	0.8	0.4	0.3	0.5
Heavy metals in mg/kg dm						
Cu	165	143	389	17.0	26	44.0
Zn	433	1870	12981	75.0	172	520
Co	21.0	19.0	17.5	2.0	1.0	< 1.0
Mo	2.8	4.2	13.2	< 10.0	< 10.0	10.0
As	4.1	6.7	37.4	< 5.0	< 5.0	22.0
Ni	66.0	59.6	63.4	4.0	< 2.5	< 2.5
Cr	326	159	231	13.5	17.5	6.8
Pb	13.6	57.6	1053	5.1	21.5	80.0
Cd	1.2	21.6	80.7	0.2	1.8	5.2
V	43.0	40.5	23.6	< 10.0	< 10.0	< 10.0
Hg	0.01	0.04	1.47	< 0.1	< 0.1	0.7

3.3.5 Measures to improve ash melting properties of biomass fuels

Elemental composition of biomass fuels is the most decisive factor with regard to composition and related properties of the respective ashes, and various measures to influence the fuel composition are frequently discussed. In the present chapter, major aspects regarding raw material selection as well as major information on the use of additives are summarised, being particularly relevant for the investigations conducted in this thesis. However, pre-treatment techniques like fractionation [e.g. ARVELAKIS 2002] or leaching [e.g. JENKINS 1996, TURN 1997, ARVELAKIS 2002, ARVELAKIS 2008] of the raw material will not be discussed.

Raw material selection, pre-treatment and processing

The main features regarding fuel composition are determined by raw material selection. Apart from the type of plant (e.g. particular types of woody, herbaceous or fruit biomass), the

respective raw material fraction is of major importance with regard to fuel properties (e.g. stem wood vs. bark vs. branches or grain vs. straw).

Raw material blending is also a topic that is frequently discussed, aiming at optimisation of biomass fuels by choosing appropriate raw materials. However, only little information on fuel and ash properties is available for blended biomass fuels (e.g. SCHMITT 2013, THY 2006 (2), WOPIENKA 2012). Moreover, hardly any results regarding the performance in real combustion application of blended fuels is found (cf. WOPIENKA 2012), thus lacking the predictability of combustion properties of unknown mixtures.

Another aspect regarding raw material quality is contamination with soil or sand: Careful treatment of storage and drying processes of raw material to avoid mineral contamination is recommended by ÖHMAN 2004 (3), since problematic behaviour of various wood pellets could be related to contamination with sand. Moreover, increased slag formation tendencies were observed as a result of sand contamination for different wood-derived biofuels by LINDSTRÖM 2008.

Use of additives

Adding mineral compounds to a biomass raw material is a frequently discussed measure to change the composition of a fuel, and consequently influence composition and thus also properties of the respective ash. Among numerous previous investigations on that topic, results from fixed bed combustion tests as well as from particular laboratory test methods (i.e. ash fusion test and simple sintering test) were considered as most relevant with regard to the subject of this thesis.

In order to improve the melting properties and slagging behaviour of biomass ashes, mainly Ca- and Al-containing additives have been investigated by numerous authors [cf. STEENARI 1998, HJULER 2002, ÖHMAN 2004 (2), LINDSTRÖM 2007, LLORENTE 2008, XIONG 2008, STEENARI 2009, BOSTRÖM 2009, SCHMITT 2013, WANG 2014], notably

- dolomite, calcined dolomite, lime (CaO , Ca(OH)_2) or limestone (CaCO_3) containing mainly Ca and/or Mg,
- kaolin, Al(OH)_3 , tabular alumina or ophtite containing Al or Al-silicates, but also
- sewage sludge and mineral residues i.e. marble sludge and clay sludge.

Effects observed for different fuel-additive-combinations

Sintering of straw could be reduced by both Ca- and Al-containing additives (cf. STEENARI 1998, SCHMITT 2013, WANG 2014), whereas kaolin was considered to be more efficient in this regard by STEENARI 1998. Moreover, melting properties could be improved by adding sewage sludge, containing Al and Si but also significant amounts of Ca and P [WANG 2014]. Also for a variety of agricultural (by-)products and residues both Ca- and Al-containing additives could increase the melting temperatures and reduce sintering respectively [HJULER 2002, LLORENTE 2008, XIONG 2008, STEENARI 2009]. STEENARI 2009 even found that the best anti-slagging effect was achieved when both additives were used. However, some investigations showed that the effect on ash melting properties is strongly dependent on the particular fuel-additive-combination; i.e. additives that improve the properties of a raw material on one hand show no

or even a reverse effect in terms of increased slag formation when applied to another biomass fuel: Slag formation of oat e.g. was prevented by adding kaolin, but was on the other hand increased by the addition of lime [BOSTRÖM 2009]. Also, improving effects of Ca-containing additives were observed compared to Al-containing additives that even worsened the melting properties of particular woody raw materials: Limestone totally eliminated severe slagging of problematic stem wood material, whereas kaolin showed only little reduction of slagging for problematic stem wood, but increased slag formation of non-problematic stem wood [ÖHMAN 2004 (2)]. Also better effects of Ca-containing marble sludge were determined when added to wood waste, and Al-containing clay sludge caused more severe slag formation [WANG 2014].

Effectiveness of different additives

In general, stronger effects with increasing amounts of a particular additive are observed [e.g. HJULER 2002, LLORENTE 2008, SCHMITT 2013, WANG 2014]. However, conclusions with regard to efficiency or reactivity of different additives are limited, since most authors usually draw a comparison referring to equal percentages of additives, thus disregarding the effective concentration of “active” elements added therewith. E.g. poorer results of dolomite and limestone compared to lime and calcined dolomite as reported in LLORENTE 2008 may be due to higher Ca-concentrations expected for these fuels.

The increase of melting temperatures on the addition of kaolin is attributed to the K-capture effect, i.e. the formation of K-Al-silicates like KAlSiO_4 and KAlSi_2O_6 that exhibit comparable high melting temperatures [e.g. STEENARI 1998].

Dolomite was found to form silicates, and no reaction between dolomite and K-compounds could be detected [STEENARI 1998]. Thus, the decrease in sintering and melt formation caused by dolomite and other Ca-containing additives is probably due to dilution or adsorption [STEENARI 1998, LLORENTE 2008].

In P-rich fuels, the addition of Ca-additives promotes the formation of various Ca-K-phosphates with high Ca/K molar ratios that exhibit high melting temperatures when compared to K-rich types of Ca/Mg-K-phosphates that are usually found in ashes of these types of biomass [LINDSTRÖM 2007].

3.4 Methods to assess the ash melting behaviour

Investigations concerning the slag formation propensity of ashes have already been conducted by the end of the 19th century, mainly dealing with coal ashes and their probability to form deposits and slag on heat exchangers [cf. BRYERS 1996]. During the last decades biomass fuels have become increasingly important for combustion processes. In this regard not only slagging and fouling (in terms of the formation of deposits) but also the formation of ash and slag lumps due to ash melting on the grate or agglomeration in fluidised bed combustion processes are of increasing interest.

Currently, the ash fusion test as described e.g. in ÖNORM CEN/TS 15370 is the only standardised method for the determination of the ash melting behaviour, described in different standards showing only little variation. The significance of this test, initially

developed for the characterisation of coal ashes, has been criticised by numerous authors [e.g. GUPTA 1998, HANSEN 1999, SKRIFVAR 1999, FRANDSEN 2003], and consequently efforts are made to find more suitable methods in order to describe the properties of ash in this regard. A large number of methods have been developed either to assess the slagging characteristics of biomass fuels or to predict the melting behaviour of the respective ashes in the combustion zone. In the following chapter, mainly methods investigating the melting properties on the grate are described. An overview is provided in Table 8, and different approaches are surveyed in the section below.

Table 8: Overview about methods for the assessment of ash melting and slagging

Approach	Method	Reference
Theoretical approaches	Indices or critical numbers e.g. Alkali-Index, Fouling Index, Acid-Base-Ratio, Silica-ratio, slagging-factor, empirical equations for viscosity or melting temperature	e.g. JENKINS 1998, PRONOBIS 2005, STOIFL 2000, SOMMERSACHER 2011
	Equilibrium calculations	e.g. ZEVENHOVEN-ONDERWATER 2001
	Ternary phase diagrams	e.g. CAPABLO 2009, PAULRUD 2001
Laboratory methods	Ash Fusion Test (AFT)	ÖNORM CEN/TS 153 70
	Improved Ash Fusion Test (ACIRL ¹ Test)	WALL 1998
	CSIRO ² Test	WALL 1998
	Thermo-mechanical Analysis (TMA-Test)	GUPTA 1998
	Melt area fraction (MAF)	HJULER 2000
	Thermogravimetric Analysis (TGA), Simultaneous Differential Thermal Analysis (SDTA), Simultaneous Thermal Analysis (STA)	HANSEN 1999
	Slag analyser	HANSEN 2008
	Compression strength test	e.g. SKRIFVAR 1998
	Fluidised bed agglomeration/controlled fluidised bed agglomeration (CFBA)	ÖHMAN 1998
	Electrical resistance/ conductivity and thermal conductivity	Al-Otoom 2000, WALL 1998
	Pressure drop technique	Al-Otoom 2000
	Simple oven method	ENGLISCH 2010
	Rapid test (DTI ³)	DAHL 2008
	CIEMAT ⁴ rapid test	LLORENTE 2005, ENGLISCH 2010
Experimental determination	Combustion experiments in combustion units under constant conditions (heat output, duration of experiment, fuel-to-air ratio)	e.g. ÖHMAN 2004 (1), LINDSTRÖM 2007, GILBE 2008 (1)

¹ Australian Coal Industry Research Laboratories

² Commonwealth Scientific and Industrial Research Organisation

³ Danish Technological Institute

⁴ Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas

3.4.1 Evaluations based on elemental composition

Numerous approaches are proposed in literature where slagging or ash melting characteristics of biomass or the respective ash are evaluated based on the elemental composition. Indices or critical numbers are calculated from one or more elemental concentrations which are considered as mainly relevant for the particular problem. Moreover, properties which are significant regarding the ash melting behaviour - like viscosity or characteristic ash melting temperatures - are estimated from the fuel properties based on empirical correlations. The state of matter of ash can also be calculated via equilibrium calculations using a set of thermodynamic data and special software. In a simplified way, the melting temperature can also be estimated using ternary phase diagrams considering the main components of the oxide mixture.

3.4.1.1 Indices or critical numbers

Slagging, fouling and deposit formation are frequently related to the so called **alkali indices** or **alkali numbers** (cf. [JENKINS 1998, MILES 1996]). These key figures are mainly calculated from the amount of the alkaline metals K and Na in the fuel related the total fuel mass, the ash or the energy content of the fuel. Another number describing the same phenomena is the **(multifuel) fouling index** [HUPPA 1983]. It is expressed by the total amount of sulphate forming elements (i.e. water soluble Ca, Mg, Na and K) in the ash. In general these indices are rather used to describe slagging in terms of the formation of deposits than the formation of slag or ash melting of bottom ash in the combustion zone.

The **base/acid-ratio** is determined via the relation of basic to acid compounds in the ash, based on the assumption that basic compounds lower the ash melting point while acid ones increase it. It is mostly based on the eight fundamental oxides most frequently found in ashes (cf. Formula 3.4.1).

$$R_{b/a} = \frac{\frac{Fe}{2} \frac{O}{3} + CaO + MgO + \frac{K}{2} \frac{O}{2} + \frac{Na}{2} \frac{O}{2}}{\frac{SiO}{2} + \frac{TiO}{2} + \frac{Al}{2} \frac{O}{3}}$$

Formula 3.4.1: Base/acid-ratio according to [JENKINS 1998]

Base/Acid-ratio.....[$R_{b/a}$] = -

Elemental conc.....[$Fe_2O_3, CaO, K_2O, \dots$] = $mg \cdot kg^{-1}$

A large number of variations can be found for the **base/acid-ratio** e.g. including the concentration of P_2O_5 [PRONOBIS 2005], referring the amount of basic oxides to the total amount of ash (instead of acid oxides), simplifying the expression by neglecting the amount of alkaline metals or titanium, or calculating the reciprocal value, i.e. the acid/base-ratio [BRYERS 1996].

According to [BRYERS 1996] the fusion temperature of coal ashes correlates with the fraction of basic oxides in a parabolic graph with a minimum at intermediate values, (for coal, a minimum is frequently located around 0.75, for biomass a minimum at lower values can be assumed.) additionally influenced by the relation of SiO_2/Al_2O_3 . Consequently, a number of correlations have been developed in order to predict the melting temperature of coal ashes.

In this regard, also other simple relations are used as reference values to assess the slag formation propensity of a fuel like e.g. the silica ratio [STOIFL 2000].

3.4.1.2 Empirical correlations

A set of empirical correlations has been developed in order to calculate **characteristic temperatures** from methods of ash characterisation like the ash fusion test (AFT) (cf. REISINGER 1993, HARTMANN 2000, FRIEDL 2004, SEGGINI 1999) or the improved ash fusion test (see 3.4.2 Laboratory methods) (cf. KAHRAMAN 1998) based on the elemental composition of the fuels or fuel ashes respectively. An overview about various correlations is provided in REISINGER 1993 and BRYERS 1996]

Empirical correlations were also developed for the determination of the **temperature of critical viscosity (t_{cv})**. This temperature indicates a point of very abrupt change in the viscosity-temperature relationship. Correlations were found between t_{cv} and characteristic temperatures of the AFT. Moreover, sensitivity of t_{cv} to surrounding atmosphere (oxidising or reducing) as well as ash composition could be observed. In this regard, the temperature of critical viscosity was described by an empirical correlation based on the ash composition in terms of the major components of coal ash (Si, Al, Fe, Ca and Mg). [VARGAS 2001]

3.4.1.3 Equilibrium calculations

Based on the chemical composition and defined surrounding atmosphere, the fraction of liquid phase in the ash is calculated at different temperatures, using special software and database. The method is based on a set of thermodynamic data, assuming an equilibrium condition, implying infinite reaction times and perfect mixing. Evaluation criterion for the assessment of the melting behaviour is the temperature where a defined amount of slag has been formed. [cf. BLANDER 1995, ZEVENHOVEN-ONDERWATER 2001, ÖHMAN 2004 (1), ÖHMAN 2004 (2), JÖLLER 2007, LINDSTRÖM 2007, GILBE 2008 (2)]

3.4.1.4 Ternary phase diagrams

In ternary phase diagrams information about the state of phases for any composition of a three component mixture are shown, and usually, liquidus or solidus temperatures are presented. Data shown in such diagrams apply to equilibrium states of a system of maximum 3 components. For multi-component mixtures like ashes, data about the elemental composition have to be simplified with regard to the main constituents, thus suffering the loss of accuracy of this technique.

Ternary diagrams are usually used to present ashes based on their elemental composition aiming at a classification e.g. with regard to melting behaviour or origin of the samples [e.g. CAPABLO 2009, LLORENTE 2005]. In some cases, ash melting behaviour is estimated based on the solidus temperatures in a diagram. [e.g. PAULRUD 2001, WALL 1998]. In Figure 8 examples for representing biomass samples in ternary diagrams are given.

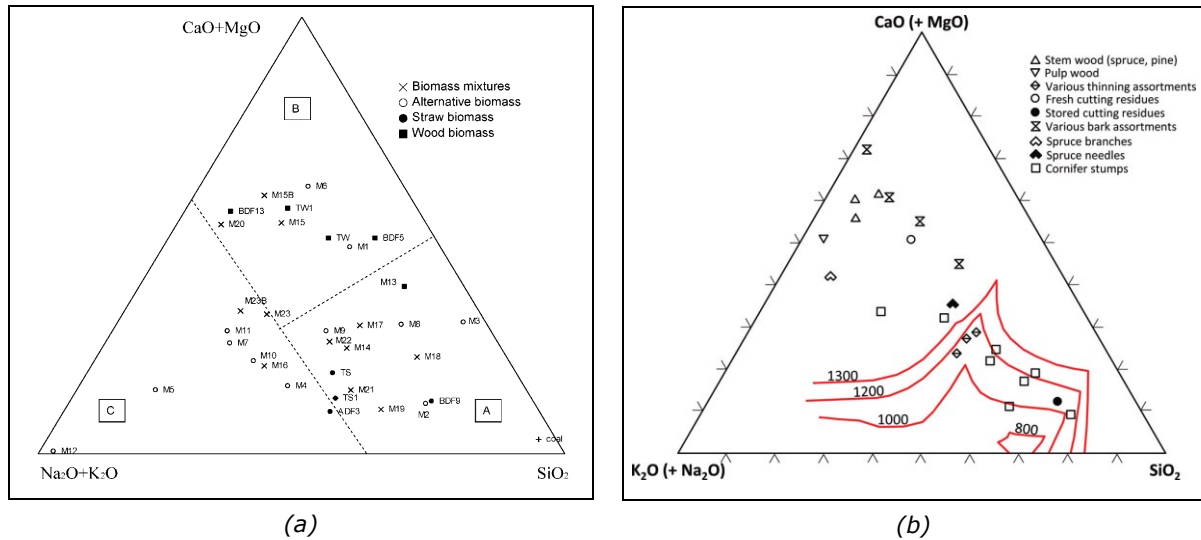


Figure 8: Presentation of different biomass samples for classification purposes (Group A: straw like fuel ashes, Group B: wood-type fuel ashes, Group C: high-alkali fuel ashes) [CAPABLO 2009] (a) and data-points representing biomass samples compared to melting curves [BOSTRÖM 2009] (b) in ternary diagrams.

3.4.2 Laboratory methods

In order to determine the melting behaviour of ashes, a number of laboratory methods have been developed. The aim is to obtain key figures from analyses or experiments in order to be able to predict the ash melting behaviour or slag formation tendency of the investigated fuel.

Besides optical evaluation, various physical properties are used for characterisation. A brief description of the available methods is given below, classified according to the respective assessment criterion.

Optical assessment of volume or shape

The **ash fusion test (AFT)** was initially set up for the determination of fusibility of coal ashes, and currently is the only standardised method available. Therefore, a small test specimen made of laboratory ash is observed continuously under a microscope while being heated up with a constant rate in a defined gas atmosphere. Temperatures where characteristic changes with regard to the shape of the specimen occur are used for the description of the ash melting behaviour.

Several variations of this method are available and also used for biomass, like e.g. DIN 51730, ISO 540 or ASTM D 1857 [HJULER 2005]. Though the procedures are very similar, the methods differ with regard to specimen shapes, preparation procedure, ash binder, particle size, heating rate but also definition of the characteristic temperatures [cf. HOUGH 1990].

In Europe DIN 51730 and the more actual European standard ÖNORM CEN/TS 15370 are most commonly used. The characteristic temperatures for the description of the ash melting behaviour according to both standards are shown in Figure 9 and Figure 11.

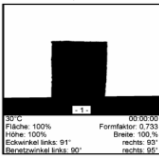
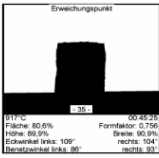
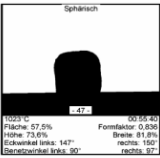
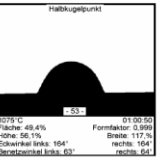
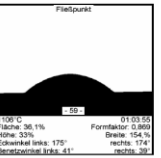
Shape						
Term	Original shape = Shape and size at 550 °C		A Softening Temperature (SOT)	B Spherical Temperature (SPT)	C Hemispheric Temperature (HT)	D Flow Temperature (FT)
Criterion			First signs of softening (rounding of edges, expanding of test specimen)	spherical height=base $H=2r$	hemispherical $H=r$	$H=1/3$ of the height at HT

Figure 9: Definition of characteristic temperatures according to DIN 51730 (H ...height, r ...base diameter).

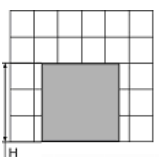
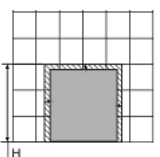
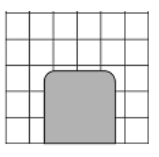
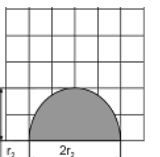
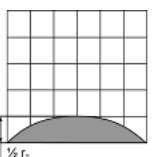
Shape						
Term		Shrinkage starting temperature (SST)	Deformation Temperature (DT)		Hemisphere Temperature (HT)	Flow Temperature (FT)
Criterion	Original shape = Shape and size at 550 °C	Area of the test piece below 95 % of the original test piece.	First signs of rounding of the edges. For computerised evaluation: shape factor change of 15 %.		Approximately hemispherical $H=r$	Ash is spread out over the supporting tile in a layer. $H=1/2$ the height at HT

Figure 10: Definition of characteristic temperatures according to ÖNORM CEN/TS 15370 (H ...height, r ...base diameter)

Another method based on optical evaluation of fuel ash is the **melt area fraction (MAF)** method, developed by dk-TEKNIK [HJULER 2000]. Therefore a few mm^3 of fuel ash are placed on a sapphire specimen disc on a heating stage, and heated up with a constant rate in a well-controlled gas atmosphere. At any time the actual area A of the silhouette of the ash sample is compared to the area of the sample in the initial image, A_0 , and samples are characterised by plotting the area fraction $(1-A)/A_0$ versus temperature. The temperatures at which the area fraction is 10 % and 50 % are used as reference point for evaluation.

Mechanical stability

Methods like the **thermo mechanical analysis (TMA)** [GUPTA 1998], the **improved ash fusion test (ACIRL)** or the **CSIRO-Test** [WALL 1998] are very similar to the AFT, but use the mechanical stability of the samples for characterisation instead of an optical evaluation. The principles of these methods are shown in Figure 11 and Figure 12.

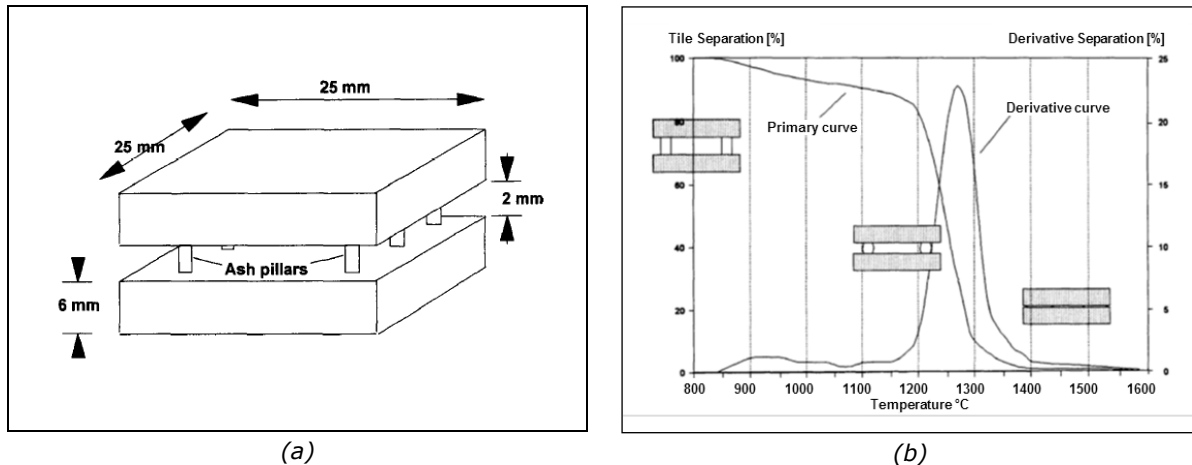


Figure 11: Experimental setup (a) and graphic response of the ACIRL-Test [KAHRAMAN 1998].

In these methods, a certain pressure is imposed upon the ash or an ash-made test body by charging ash-made pillars with a ceramic tile (ACIRL) or placing a penetrating ram in a crucible filled with ash (TMA, CSIRO). The progressive loss of mechanical stability is determined continuously while the samples are heated up. The shrinkage of the sample is quantified based on the distance between the ceramic tiles or the penetration depth respectively referring to the initial position, and plotted versus temperature. For the characterisation of the sample, temperatures with a maximum change or temperatures at a certain state of shrinkage are identified. [GUPTA 1998, WALL 1998, BRYANT 2000]

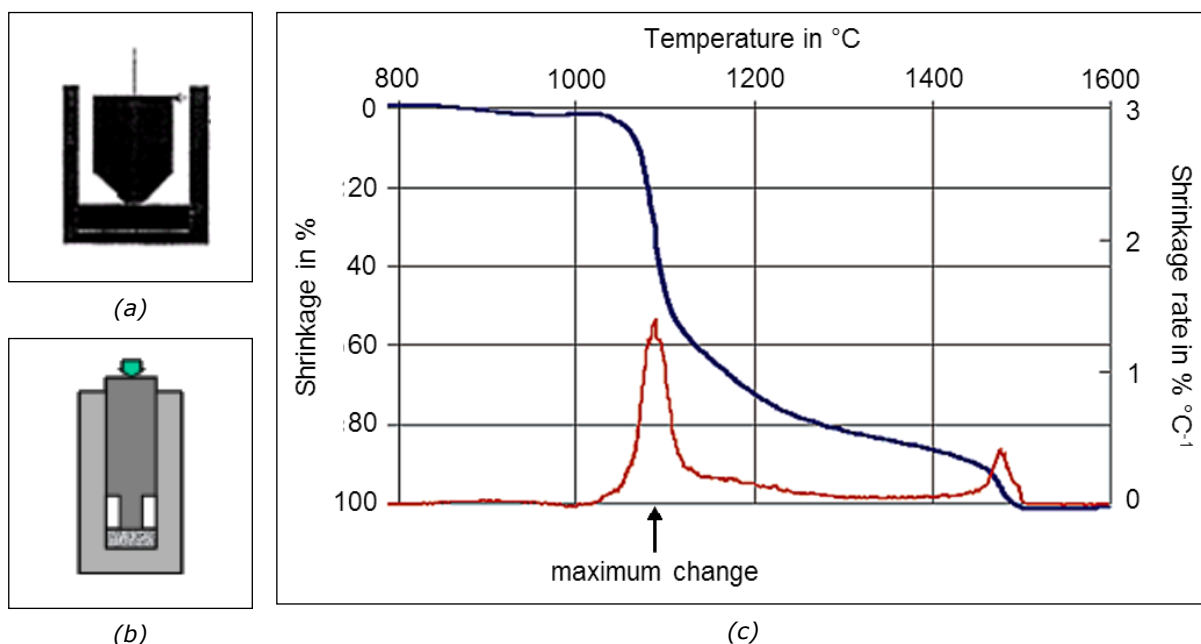


Figure 12: Basic principle of the CSIRO-Test [WALL 1998] (a) and TMA-Test [GUPTA 1998] (b), and graphic response of TMA-Test [GUPTA 2007] (c).

Another method based on the mechanical stability of the test specimen is the **compression strength test**. For a defined period ash pellets are exposed to a certain temperature and cooled down again. Dimensions and compressive strength of the ash pellets are evaluated,

and the compression strength is taken as a measure for the amount of sintered or molten material. For evaluation the compression strength is plotted vs. temperature, and the range where the pellets start to increase their strength is determined. [cf. SKRIFVARS 1998, TANGSATHITKULCHAI 2001]

Several variations of relatively fast **oven test methods** exist, where the mechanical stability of ash samples is also evaluated, resulting from small amounts of fuel or fuel ash that are exposed to different temperatures in a laboratory oven for a given period of time. This is done either in a qualitative way by manual disintegration or by sieving (cf. Simple oven method by ofi [ENGLISH 2010], Rapid test (DTI) [DAHL 2008] or CIEMAT rapid test [LLORENTE 2005, ENGLISH 2010]).

Electrical and thermal conductivity

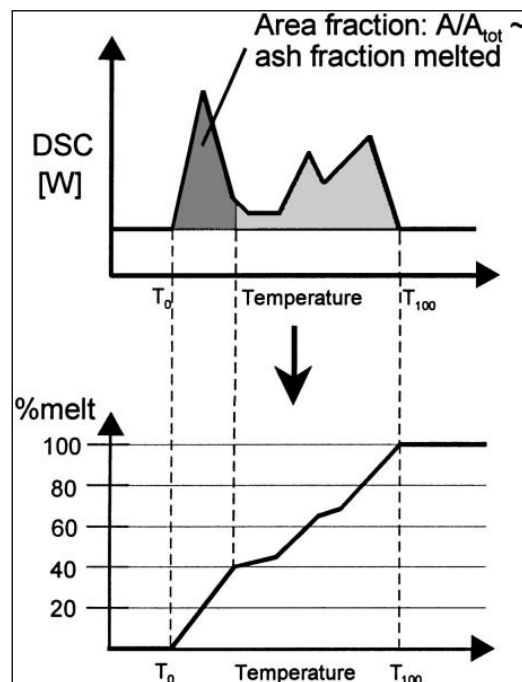
The degree of ash sintering and fusion is determined by measuring the electrical resistance of a pellet made of fuel ash, characterising the conduction path through the layer and thus, particle-particle contact and fusion. [WALL 1998]

A similar method is to use thermal conductivity to determine the sintering temperature of ash. Due to ash sintering more connections between the particles are formed, and the effective contact surface area for conduction is increased. As a result, the rate of thermal conductivity with respect to temperature starts to increase. [AL-OTOOM 2000]

Enthalpy of reaction or transformation

Phase changes are determined via thermal analyses like **Thermo gravimetric Analysis (TGA)**, **Simultaneous Differential Thermal Analysis (SDTA)** or **Simultaneous Thermal Analysis (STA)**. Mass changes and heat consuming or producing reactions are detected while the ash sample is heated up continuously, and melting is detected as an endothermic process involving no change in mass. Signals from STA can be transferred to melting curves based on the DSC signal. This can be done by either measuring the percentage of melting energy referring to the energy required for the total melting process, or by evaluating the signals identifying the respective species melting [HANSEN 1999].

Figure 13: Conversion of STA curves to melt curve
[HANSEN 1999]



Pressure drop

In order to determine the sintering temperature, an ash pellet is prepared and compressed in an alumina tube. This tube is heated up constantly from the ambient temperature to 1000 °C while air passes through with a constant flow rate, and the temperature of the ash pellet as well as the pressure-drop across it are recorded continuously. When sintering occurs, the pellet starts to shrink and thus pulls away from the wall of the alumina tube, forming new

pathways for the passage of air. Therefore, the sintering temperature is obtained from the point of maximum pressure-drop. [AL-OTOOM 2000]

Quality, size and percentage of slag particles in the ash

Several methods have been developed where standard experiments are conducted using a specified procedure and evaluation technique. Most commonly, residual ash is evaluated with regard to size and percentage of slag particles formed. [e.g. ÖHMAN 2004 (2)]

The Danish Technological Institute (DTI) e.g. developed a **slag analyser**, in which solid biofuels are burnt under controlled conditions, and from which ash and slag are collected for analyses. Combustion residues are evaluated following a categorisation with regard to the percentage of slag on the grate and the walls of the combustion chamber, the percentage of molten particles of a certain size, the percentage of all slag referring to the initial fuel mass and the size of the largest slag particles on the grate. [HANSEN 2008] Moreover, further development of this method is part of an ongoing project dealing with the development of a reliable ash melting method [SCHWABL 2013].

Defluidisation temperature

Controlled fluidised bed agglomeration CFBA - a method using a bench scale fluidised bed reactor – was developed by Umeå University [ÖHMAN 1998]. The method is based on the controlled increase of the bed temperature by applying external heat to the primary air and to the bed section walls. The bed is loaded with a certain amount of ash from previously burnt fuels under combustion atmosphere. The initial agglomeration temperature is determined by on- or off-line principal component analysis of the variations in measured bed temperatures and differential pressures.

3.4.3 Experimental evaluation in small-scale combustion units

Some work has been done investigating the slag formation and ash melting behaviour respectively conducting practical experiments in small-scale combustion units. The consideration of these experiments as methods is acceptable, since the experimental work is conducted using standardised procedures and evaluation criteria.

Frequently, the ash melting behaviour is only assessed by documenting if no, little or large amounts of slag have been formed on the grate after a combustion experiment. In some publications this system is improved by setting up a classification of the combustion residues based on defined properties. Qualitative evaluation e.g. has been conducted by classifying ash residues in categories based on visual and microscopy inspection, assessing the sintering degree as well as the size of molten blocks [cf. ÖHMAN 2004 (1), ÖHMAN 2004 (2), LINDSTRÖM 2007, LINDSTRÖM 2008, GILBE 2008 (1), GILBE 2008 (2), XIONG 2008]. In some cases, quantitative evaluation is done by determining the fraction of total ash that formed slag, separated by sieving [GILBE 2008 (1), GILBE 2008 (2), LINDSTRÖM 2008]. The degree of slag formation is sometimes also quantified by determining the share of amorphous i.e. formerly molten material in the ash [e.g. ÖHMAN 2004 (1), GILBE 2008 (1), LINDSTRÖM 2008] by XRD-analyses. Moreover, the identification of mineral phases or compounds can provide qualitative information about formation mechanisms or the effect of single compounds [GILBE 2008 (1)].

4 Materials and Methods

The experimental work for this thesis was done in the context of different projects. Thus, a number of aspects were considered when choosing raw materials, additives and combustion appliances. The following section provides an overview of the total of materials used and the experimental program. Analysis methods for fuel and ash are described, as well as the method used for slag evaluation. Moreover, statistical terms and definitions used in the present thesis as well as methods applied for multivariate data analysis are briefly explained.

4.1 Fuels

In order to ensure a broad variety of fuel properties different types of woody and non-woody biofuels have been chosen. Table 9 gives an overview about the investigated fuels.

Table 9: Raw materials used and number of samples investigated per fuel

Raw material		Number of samples		
		pure	with additive	total
High-quality wood pellets	Spruce	5	0	5
	Spruce with organic binder (starch, meal of rye or maize)	12	0	12
	Larch	1	0	1
	Pine	1	0	1
Low quality wood pellets	Spruce with bark	2	0	2
	Wood (no detailed information about raw material basis available)	15	0	15
Mixed pellets	Wood mixed with 40 % corn cob residues	1	0	1
	Wood mixed with 10 % straw	1	0	1
Non-woody / agricultural biomass	Maize whole crop	3	1	4
	Miscanthus	9	2	11
	Straw	11	29	40
	Energy grain	7	4	11
	Hay	6	0	6
	Cereal whole crop, corn cob residues, foliage, rape seed cake, giant reed, sorghum bicolor, wheat bran, vine pruning	1 ^{*)}	0	1

^{*)} one sample each fuel

According to the type of raw material and product quality, the investigated fuels can be classified as follows:

High-quality wood pellets have been specially produced by Austrian pellets manufacturers from defined raw materials under well-controlled conditions.

Low quality wood pellets were obtained from all over Europe, focusing on potentially problematic qualities with regard to ash melting and slag formation. For these fuels no or only

little information (from interviews with the pellets manufacturers) about raw material and production process are available.

Non-woody biomass was mainly obtained from different Austrian farmers. The major part of these fuels was pelletised in cooperation with an Austrian straw pellets manufacturer under well-controlled conditions. In some cases biomass was used as chipped material.

Additives and binders

Pellets have either been produced from pure raw material or using organic binders or mineral additives aiming at an improvement of the fuel quality. Moreover, pellets have been produced mixing woody and non-woody materials. In Table 10 organic binders and mineral additives are listed including their main constituents.

Table 10: Overview about organic and mineral additives used for pellets production

Type of additive		Main compound(s)
Organic material	Starch	Starch (carbohydrate)
	Maize, coarse meal	carbohydrates, proteins
	Rye flour	carbohydrates, proteins
Ca- and/or Mg-containing mineral additives	Lime	CaO
	Carbonate of lime	mainly CaCO_3
	Dollit TM	CaCO_3 and MgCO_3
	Epsomite	MgSO_4
	Magnesiummehl TM	CaCO_3 and MgCO_3
Al-containing mineral additives	Mullite	$\text{Al}_4\text{Si}_2\text{O}_{10}$
	AlSiH TM	Si-Al-compound (Si:Al ~ 1:1)
	Sialin TM	Si-Al-compound (Si:Al ~ 1:5)
	Bauxite (Al- and Fe-minerals)	Oxide/Hydroxide of Al, Fe, Si
	Bentonite	Silicate of Al, Mg and Na

The range of particular fuel properties for the different fuels investigated is presented in Table 11, summarising fuels with and without additives. Moreover, the distribution of ash content according to the number of samples is shown in Figure 14 to exemplify the variation range of the investigated fuels. Detailed analyses results for all fuels are listed in Annex IV – Properties of fuel and ash samples.

Table 11 (Part A): Variation range of fuel properties of the investigated fuels (High-quality wood, low-quality wood, grain and hay.

Raw material	High-quality wood	Low-quality wood	Grain	Hay
Ash in %	0.21 – 0.36	0.26 – 2.06	1.13 – 8.03	6.00 – 11.20
Net calorific value $q_{p, net, d}$ in MJ/kg	18.56 – 19.02	18.19 – 19.20	15.51 – 17.73	16.21 – 17.74
Volatile matter in %	83.6 – 85.2	80.8 – 85.2	77.6 – 83.8	71.2 – 74.6
C in %	49.8 – 51.5	48.7 – 53.3	41.4 – 46.4	42.2 – 46.2
H in %	5.56 – 5.97	5.91 – 6.39	5.60 – 6.76	5.37 – 5.91
N in %	0.10 – 0.30	0.12 – 0.39	1.35 – 2.45	0.90 – 1.65
Al in mg/kg	15 – 30	12 – 840	6 – 36	550 – 6480
Ca in mg/kg	760 – 920	450 – 2780	61 – 3810	3840 – 7100
Cl in mg/kg	16 – 46	18 – 170	390 – 1500	1090 – 3470
Fe in mg/kg	7 – 30	15 – 580	25 – 75	520 – 2280
K in mg/kg	270 – 560	220 – 1440	3260 – 6620	10200 – 20700
Mg in mg/kg	110 – 200	67 – 440	1020 – 1470	660 – 2460
Mn in mg/kg	88 – 180	47 – 200	6 – 43	85 – 340
Na in mg/kg	10 – 15	6 – 150	13 – 120	200 – 1530
P in mg/kg	20 – 240	28 – 87	2720 – 4260	1440 – 2460
S in mg/kg	37 – 110	32 – 180	1010 – 1700	1010 – 1730
Si in mg/kg	7 – 77	110 – 3340	160 – 3370	5770 – 36400
Ti in mg/kg	0 – 0	2 – 100	2 – 120	130 – 720
Zn in mg/kg	5 – 11	5 – 18	20 – 34	20 – 42

Table 11 (Part B): Variation range of fuel properties of the investigated fuels (Maize whole crop, Miscanthus, Straw and various other biomass fuels.

Raw material	Maize whole crop	Miscanthus	Straw	Other
Ash in %	2.83 – 6.31	1.99 – 6.62	5.10 – 12.90	0.83 – 6.30
Net calorific value $q_{p, net, d}$ in MJ/kg	16.76 – 17.75	17.10 – 18.15	15.97 – 17.60	17.46 – 18.76
Volatile matter in %	78.9 – 81.7	79.6 – 82.9	71.6 – 76.2	75.3 – 82.8
C in %	44.6 – 47.5	46.9 – 51.0	44.7 – 48.5	41.1 – 50.5
H in %	5.94 – 6.32	5.65 – 6.13	5.11 – 6.13	5.83 – 6.76
N in %	0.76 – 1.20	0.09 – 0.29	0.35 – 0.66	0.16 – 5.15
Al in mg/kg	110 – 350	53 – 11600	110 – 10500	10 – 210
Ca in mg/kg	940 – 8100	810 – 9300	1900 – 10900	410 – 6850
Cl in mg/kg	650 – 1020	130 – 650	570 – 5120	210 – 3390
Fe in mg/kg	110 – 310	79 – 790	85 – 2710	43 – 1090
K in mg/kg	4810 – 8130	990 – 3700	6380 – 15700	1290 – 15100

Table 11 (Part B, continuation): Variation range of fuel properties of the investigated fuels (Maize whole crop, Miscanthus, Straw and various other biomass fuels.

Raw material	Maize whole crop	Miscanthus	Straw	Other
Mg in mg/kg	1070 - 4760	290 - 4960	540 - 4420	180 - 4590
Mn in mg/kg	15 - 24	25 - 68	13 - 91	8 - 120
Na in mg/kg	26 - 100	19 - 150	33 - 680	21 - 550
P in mg/kg	1800 - 2000	170 - 560	400 - 720	80 - 10100
S in mg/kg	810 - 1060	330 - 520	530 - 1200	150 - 6240
Si in mg/kg	3380 - 4690	4570 - 9830	8420 - 29200	100 - 9050
Ti in mg/kg	32 - 160	11 - 980	52 - 1060	1 - 250
Zn in mg/kg	17 - 21	8 - 21	3 - 8	11 - 76

Almost all wood pellets have an ash content below 1 %, only exceeded by 3 samples, and the ash content of all high-quality wood pellets is found below 0.5 %. The values for most non-woody biomass fuels are distributed in the range of 1 % – 10 %, and 5 samples even exceed that value.

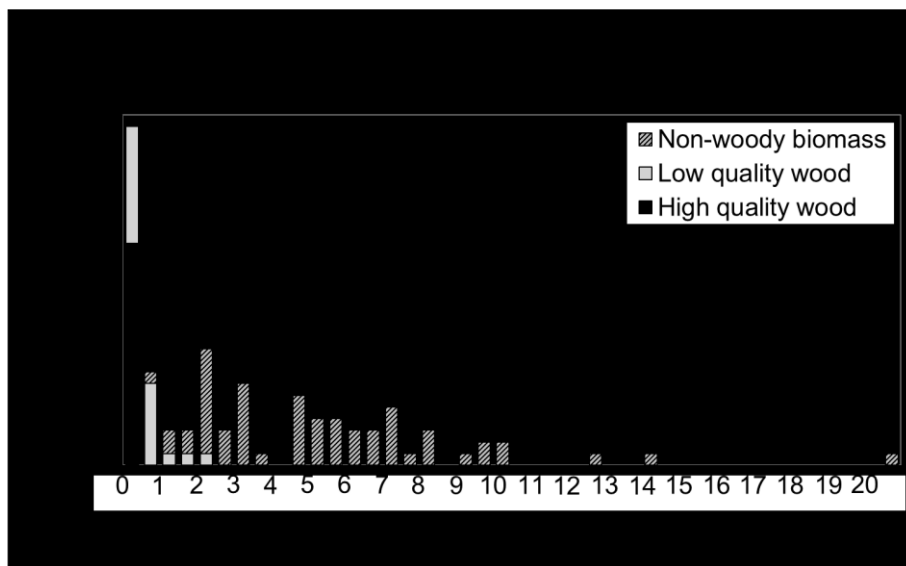


Figure 14: Number of fuel samples representing a particular ash content

4.2 Combustion units

Boilers used for laboratory experiments were chosen in order to investigate different types of ash removal technologies, combustion chamber material, fuel feeding systems and control strategies, and their impact on slag formation in the combustion zone. Table 12 gives an overview about the investigated boilers and their main characteristics.

The investigated combustion units cover a power range of 10–31 kW. For the selection of the combustion units both grate section and ash removal solution were important. Systems with a moving or tilting grate were chosen expecting a more efficient ash/slag transport. In the

underfeed burners, the grate is designed like a plate, and combustion residues are only transported by the successive fuel. Higher demands on the fuel quality are made by the burner pot with a perforated plate on the bottom: Ash is either entrained with the combustion air or through the wholes in the plate when opening the valve, and thus only fine ash or very small slag particles can be removed. In addition a stove was tested with a grating that requires manual cleaning. Combustion chamber material was either metal or refractory material. All different types of fuel feeding were considered i.e. top feed, under feed and fuel feeding from the side. Regarding the control strategy both temperature controlled and lambda controlled solutions are used.

Boilers used for laboratory experiments are basically all dedicated to woody biomass fuels, and no design modifications were made except the application of an additional agitator to facilitate ash removal in boiler L8. For particular boilers control settings were adapted to the application of non-woody biomass on one hand, but also to investigate the impact of particular parameters like e.g. grate cleaning intervals.

Table 12: Overview of combustion units and their main characteristics

No.	Boiler (model, manufacturer)	Nominal heat load in kW	Type of grate/ash removal system	Combustion chamber material	Fuel feeding	Control strategy
L1	Windhager PMX	15	Pot with perforated plate on the bottom, ash is either entrained with the combustion air or through the wholes in the plate when opening the valve	Metal	Top feed	Temperature
L2	Windhager PMX 2.0	15	Pot with perforated plate on the bottom, ash is either entrained with the combustion air or through the wholes in the plate when opening the valve	Metal	Top feed	Temperature
L3	Fröling P3	10	Moving grate	Refractory material	Top feed	Lambda probe
L4	HET thermocomfort	31	Tilting grate	Refractory material	Horizontal feed	Lambda probe
L5	ÖkoFen Pellematic	15	Underfeed burner with a grate designed like a plate, ash/slag is transported by the successive fuel (no forced transport)	Metal	Under feed	Temperature
L6	Calimax Twist 80/20	10	Grating that requires manual cleaning	Refractory material	Top feed	Temperature
L7	KWB USV 25	25	Underfeed burner with a grate designed like a plate, ash/slag is transported by the successive fuel (no forced transport)	Metal	Under feed	Lambda probe
L8	Hargassner HSV 15	15	Moving grate with additional mechanical cleaning device	Refractory material	Horizontal feed	Lambda probe

4.3 Experimental set up and program

Combustion experiments were conducted in different types of combustion units at laboratory test facilities of BIOENERGY2020+ GmbH as well as test facilities of company partners. Moreover, additional fuel samples were investigated via fuel analyses, and no combustion tests were conducted for these fuels. This was particularly done for investigating the impact of additives. Table 13 gives an overview about the experimental program. The following aspects have been considered when setting up the experimental program:

Comparing boiler technologies: A set of different boiler types was operated with the same fuels in order to compare the respective applicability of the different technologies. Different technologies were used for woody and non-woody biomass fuels, allowing for different requirements dependent on the fuel properties.

Comparing biomass fuels: Particular boilers - L1/L2 for wood pellets and L8 for non-woody biomass – were defined as reference systems to investigate and compare different fuels under comparable conditions.

Table 13: Overview of the experimental program and number of samples investigated either in combustion tests or analysed only. (R_{HQ} , R_{LQ} and R_{NW} are reference boilers for high quality wood, low quality wood and non-woody fuels respectively).

	Number of fuels tested in each boiler								Comb. tests	Analyses only	Samples total
	L1 R_{HQ}	L2 R_{LQ}	L3	L4 ^{#)}	L5 ^{#)}	L6	L7	L8 R_{NW}			
High-quality wood	10	1 ^{o)}	5	5	6	6	1 ^{o)}	1 ^{o)}	11	8	19
Low quality wood	5	9	5	3	4	3	-	-	14	3	17
Straw ^{*)}	-	-	-	-	4	5	4	2	5	35	40
Miscanthus ^{*)}	-	-	-	-	2	4	1	4	8	3	11
Maize whole crop ^{*)}	-	-	-	-	3	3	1	2	3	1	4
Grain ^{*)}	-	-	-	-	-	-	-	-	-	1	11
Hay	-	-	-	-	-	-	-	6	3	3	6
Other ^{+))}	-	2	-	-	-	-	-	4	6	2	8

#) boilers tested at test facilities of company partners

*) with and without additive

+) e.g. wheat bran, vine yard pruning, etc. (including blends)

o) Reference fuel

4.3.1 Test procedure

Experiments were conducted under well-controlled conditions in order to receive reproducible and comparable results: Combustion units were operated at factory settings, and tests were conducted under full-load operation, i.e. at maximum possible heat load. Details on test duration as well as eventual adaptations with regard to boiler settings are described under *test procedure* for the particular test series in the following section.

During the whole test, temperature on the grate/in the fuel bed and in the combustion chamber were measured and recorded continuously. The heat output was determined based

on feed- and return flow-temperature and volume flow of the feed of the heat exchanger. Moreover, flue gas composition as well as flue gas temperature and chimney draught were recorded for additional monitoring of the combustion process. Measuring positions are shown in Figure 15 and details on measuring instruments and principles are given in Table 14.

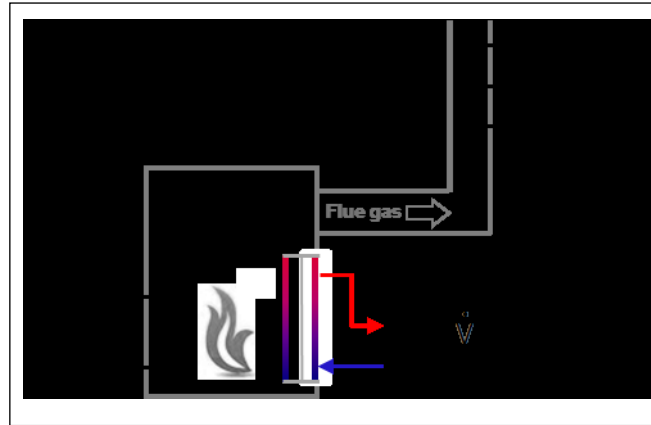


Figure 15: Schematic drawing of the experimental setup with measurements points.

Table 14: Measuring instruments and principles

Parameter	Measurement instrument / principle	Measurement range and accuracy
T_{CC}, T_{FB}	Thermocouple (Type K, class 1)	-40 °C to +1 000 °C; 0.004 * t resp. ± 1.5 °C
$T_{FG}, T_{feed}, T_{return}$ flow	Resistance thermometer (Pt 100, Type A)	0 °C to +600 °C; $\pm (0.15 + 0.002 * t)$
dp_{ch}	Pressure transmitter, inductive	0 - 50 Pascal; 0.04 % / °C (+10 to +50 °C)
\dot{V}_{Feed}	Flow meter, magnetic-inductive	0 - 30 l/s; ± 0.5 % MV
O_2	Paramagnetic	0 to 25 vol.%; ± 1 % MV
CO_2 CO NO_x	NDIR	0 - 25 vol.%; ± 0.5 % MV 0 - 3100 ppm; ± 0.5 % MV 0 - 2500 ppm; ± 0.5 % MV

After the test, ash samples were taken from the bottom ash and heat exchanger ash for further evaluation (cf. section 4.4 Evaluation of ash and slag).

4.3.2 Description of test series

Three different types of test series have been conducted at the laboratory test facilities investigating high-quality wood pellets, problematic wood pellet qualities from all over Europe and different types of non-woody biomass:

Wood pellets test series I (mainly high-quality wood pellets)

A comprehensive test series was conducted with high-quality wood pellets: Boiler L1 was defined as reference unit where all samples (10 high-quality and 5 low quality wood samples) were tested, and selected samples were also investigated in 4 other combustion appliances.

Test procedure: All 5 boilers were run at full-load operation using factory settings. Boilers L1, L3 and L5 were operated for a period of 72 h per test, whereas the standard test for boiler L4 and L6 lasted 3 h and 7 h respectively. Additional tests with reduced primary air supply were conducted in boilers L3 and L4. Table 15 gives an overview about the experimental program conducted with wood pellets of test series I.

Table 15: Overview about the experimental program conducted with wood pellets of test series I

Unit	Number of fuels tested		Full-load operation	Additional tests
	HQ wood	LQ wood		
L1	10	5	72 h	-
L3	5	5	72 h	72 h with reduced primary air supply (for 5 HQ- and 2 LQ-wood samples)
L4	5	3	3 h	3 h with reduced primary air supply for all fuels tested in boiler L4
L5	6	4	72 h	-
L6	6	3	7 h	-

Wood pellets test series II (mainly problematic wood pellet qualities)

A further test series was conducted focusing on problematic wood pellet qualities from the European market (13 samples). The same type of boiler as in the first test series was taken as reference boiler (L2 is the successor model of boiler L1), and different grate cleaning intervals were tested for each fuel.

Test procedure: A standard test procedure was defined with full-load operation for a period of 6 hours. In order to evaluate the slag formation tendency 4 different grate cleaning settings were applied with intervals of 80, 140, 200 and 360 minutes respectively.

Test series with non-woody biomass fuels

4 different units were used for combustion tests with selected non-woody biomass fuels, and the main part of the samples was tested in boiler L8.

Test procedure: Standard tests at full-load operation were conducted with all boilers. In addition, boiler settings were varied in terms of grate cleaning intervals in boiler L8. Boilers L5 and L7 were operated for a period of 24 h. Due to limitations regarding the size of the ash box the experimental duration was reduced to 12 h for boiler L8. Moreover, the experimental duration in boiler L6 was reduced to 4 h since frequent manual cleaning and consequently high personnel efforts were required.

4.4 Evaluation of ash and slag

4.4.1 Terminology of combustion residues

Laboratory ash

Ash that is produced in a laboratory oven under well controlled conditions according to ÖNORM CEN/TS 14775 (at 550 °C) or according to DIN 51719 (at 815 °C) respectively.

Combustion ash

Ash that is received from practical tests in state of the art combustion units. Further differentiation is made into bottom ash (BA) and heat exchanger ash (HE) as described in the following section.

Slag (SL)

Lumps or larger particles that result from fusion or sintering of ash in the grate section of a boiler.

4.4.2 Ash and slag sampling

The total amount of ash was collected after the combustion test, and sample reduction was achieved by partitioning of the sample. Samples were taken from both bottom ash and ash from the heat exchanger zone.

Bottom ash/slag (BA/SL)

Bottom ash terms combustion residues, which accumulate in the grate section of the boiler. Dependent on the boiler technology, bottom ash samples are taken from the ash container and/or the grate section of the boiler. Sieving analyses for quantitative evaluation of slag formation were conducted with the total amount of combustion residues. For fuel analyses, a smaller sample was generated by sub-sampling. Unless otherwise noted, analyses were conducted with homogenized samples of the whole combustion residues, including ash and eventual agglomerates or slag.

Heat exchanger ash (HE)

Heat exchanger ash terms ash that accumulates in the heat exchanger section of a boiler and/or is deposited on the heat exchanger surface, but still easy to remove by the common heat exchanger cleaning device.

In Figure 16 sampling positions are shown exemplarily for two different boiler types: Separate areas for sampling bottom ash and heat exchanger ash are accessible e.g. in boiler L1, whereas in some units the heat exchanger is situated above the grate section (cf. boiler L7 as shown in Figure 16 (b)). In this case, a large sheet of paper was inserted to collect the ash that was removed from the heat exchanger by extra cleaning movements.

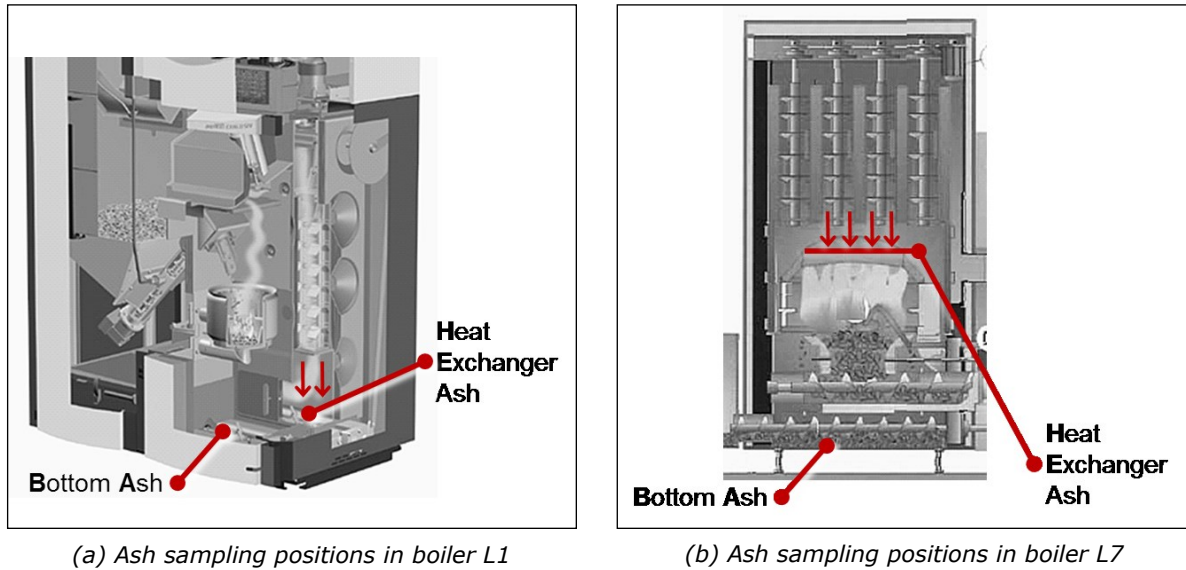


Figure 16: Ash sampling positions in boiler L1 and boiler L7.

4.4.3 Assessment of slag formation

Qualitative description

Photos were taken of ash and slag formed, and properties and conditions are described in a qualitative way in terms of e.g. density, mechanical stability, stickiness, colour and structure (e.g. porous or molten).

Semi-quantitative evaluation

The amount of slag formed is described using a semi-quantitative grading into severe slag formation (●●), considerable slag formation (●), little slag formation (○) and no slag formation (-). *Severe slag formation* is indicated if the major part of combustion residues is slag, and large agglomerates are formed on the grate thereby affecting the combustion process. The grade *considerable slag formation* is used if combustion residues consist of both ash and slag, comprising slag particles of a few centimeters though. In both cases, considerable problems are expected for long-term operation. However, *little slag formation* is indicated for ash containing only single particles in the size of a few millimeters.

Quantitative evaluation

Quantitative evaluation was done by weighing all ash and slag fractions, and calculating the respective percentage referring to the total amount of combustion residues. The slagging intensity is evaluated considering both the fraction of particles $> 5.6 \text{ mm}$ and the fraction of particles $5.6 \text{ mm} > x > 4 \text{ mm}$.

Sieving is done in an automatic sieving machine using constant parameters (*Fritsch Analysette 3*, duration 3 min, interval 10 s, amplitude 0.5 mm). Applying this procedure, loose agglomerates are destroyed and only stable slag lumps remain and are considered as slag.

4.5 Methods for fuel and ash analysis

Combustion relevant fuel properties were determined according to the methods defined in ÖNORM M 7135 and ÖNORM EN 14961-1 respectively. A brief description of each method is given below.

Ash content

The ash content is given in mass percentage referring to the dry sample. The analyses were conducted according to ÖNORM CEN/TS 14775 at 550 °C. In addition some analyses were made at 815 °C according to DIN 51719 for means of comparison. Each sample was analysed at least twice and the average value of the results is presented.

Water content

The water content is determined according to ÖNORM CEN/TS 14774-2, and is given in mass percentage of water referring to the wet mass of the sample. Each sample is analysed twice, and the average value of the results is presented.

Heating value

The Higher Heating Value (HHV or gross calorific value) and the Lower Heating Value (LHV or net calorific value) are given in MJ per kg, and results are presented referring to the dry sample. According to ÖNORM CEN/TS 14918, the HHV is determined using an adiabatic bomb calorimeter. Knowing the hydrogen content of the sample, the LHV can be calculated based on these results. Each sample is analysed at least twice and the average value of the results is presented.

Volatile matter

The amount of volatile matter in the fuel is given in percent mass referring to the dry sample. The analysis is done according to ÖNORM CEN/TS 15148. Each sample is analysed at least twice and the average value of the results is presented.

Major elements (C, H, N)

The main constituents carbon, hydrogen and nitrogen are determined according to ÖNORM CEN/TS 15104, and are given in mass percentage referring to the dry basis. For the analysis, an "elemental analyser" is used. In this apparatus, a small amount of the sample (~2-3 mg) is oxidised with an excess of oxygen. The resulting products – CO₂, H₂O und NO_x – are quantified after an adequate conversion and purification.

Sulphur and chlorine

Sulphur and chlorine are determined according to ÖNORM CEN/TS 15289. The sample is milled to fine particles, mixed thoroughly and pressed to pellets. These pellets are burned with an excess of oxygen and with the help of catalytic surfaces. The resulting gases are dissolved in deionised water and the solution is analysed via IC.

Cations – ash forming elements

Ash forming elements are determined according to ÖNORM CEN/TS 15290 and ÖNORM CEN/TS 15297. The sample is milled to fine particles and undergoes a microwave digestion using a mixture of HNO₃, H₂O₂, HF und HCl. The analyte concentration in the

resulting solution is determined via ICP-OES (Inductively coupled plasma optical emission spectrometry). Sodium is analysed via FAAS (Flame atomic absorption spectroscopy).

Ash melting behaviour

The ash melting behaviour is determined according to DIN 51730. The ash is produced according to ÖNORM CEN/TS 14775 and pressed to a small geometric body. This sample is heated up under a microscope with a certain rate and changes with regard to the shape of the sample are observed. The ash melting behaviour is described by characteristic temperatures measured at specified stages of the melting process which are termed A Softening Temperature (SOT), B Spherical Temperature (SPT), C Hemispheric Temperature (HT) and D Flow Temperature (FT).

4.6 Determination of elemental release

Due to ash reactions and volatilisation of particular elements during combustion the total amount of inorganic compounds as well as proportions and percentages in fuel and bottom ash are different. In order to be able to compare the particular elemental concentrations in the ash to the initial concentration in the fuel, analysis results are normalised to the concentration of a stable element, which is assumed not to be released during combustion. This calculation procedure has previously been applied e.g. by THY 2006 (1) relating to CaO and SiO₂ and MISRA 1993 using Ca.

For present thesis Ca was chosen as reference element, and the following aspects were taken into account:

- No elemental release is expected for Ca during combustion which is confirmed e.g. by THY 2000.
- Ca is available in all fuels in sufficient concentrations to reduce a potential impact of variations and measurement errors.
- The analytical method for the quantification of Ca is well-developed, and no major error margin for the method is expected.

Ca-based concentration of a species in the fuel and the ash is calculated according to the formulas below:

$$C_{X, \text{Ca base}, \text{fuel}} = \frac{C_{X, \text{fuel}}}{C_{\text{Ca}, \text{fuel}}} \quad \text{Formula 4.6.1}$$

and

$$C_{X, \text{Ca base}, \text{ash}} = \frac{C_{X, \text{ash}}}{C_{\text{Ca}, \text{ash}}} \quad \text{Formula 4.6.2}$$

Ca-based concentration of X in fuel..... $[C_{X, \text{Ca base}, \text{fuel}}] = \text{mg} \cdot \text{mg}^{-1}$
 Concentration of X in the fuel..... $[C_{X, \text{fuel}}] = \text{mg} \cdot \text{kg}^{-1}$
 Concentration of X in the fuel..... $[C_{\text{Ca}, \text{fuel}}] = \text{mg} \cdot \text{kg}^{-1}$

Ca-based concentration of X in ash..... $[C_{X, \text{Ca base}, \text{ash}}] = \text{mg} \cdot \text{mg}^{-1}$
 Concentration of X in the ash..... $[C_{X, \text{ash}}] = \text{mg} \cdot \text{kg}^{-1}$
 Concentration of X in the ash..... $[C_{\text{Ca}, \text{ash}}] = \text{mg} \cdot \text{kg}^{-1}$

Accordingly, the residual fraction of a particular element in the ash (X_{res}) and the corresponding released fraction (X_{rel}) are determined as follows.

$$X_{res} = \frac{C_{x,Cabase,ash}}{C_{x,Cabase,fuel}} \cdot 100 \quad \text{Formula 4.6.3}$$

and

$$X_{rel} = 1 - \frac{C_{x,Cabase,ash}}{C_{x,Cabase,fuel}} \cdot 100 \quad \text{Formula 4.6.4}$$

Residual fraction of X in ash.....[X_{res}] = %Released fraction of X.....[X_{rel}] = %

4.7 Terms and definitions of descriptive statistics

Tukey Box Plot

Tukey box plots provide information about several sample characteristics of the observations contained in a data set. The median is typically represented by a circle or a horizontal line within the box. The upper and lower sides of the box indicate the values of the upper and the lower quartiles, respectively. The distance between these quartiles is called the interquartile range; 50 % of the data are located within this range. Another feature of the Tukey box plot is the adjacent values. The upper adjacent value is defined as the largest observation less than or equal to the upper quartile plus 1.5r. The lower adjacent value is defined as the smallest observation greater or equal to the lower quartile minus 1.5r. If an observation has a value outside the adjacent values, the observation is called an outside value and is shown in the box plot by a single point. [FABER 2012]

The above described characteristics are illustrated in Figure 17.

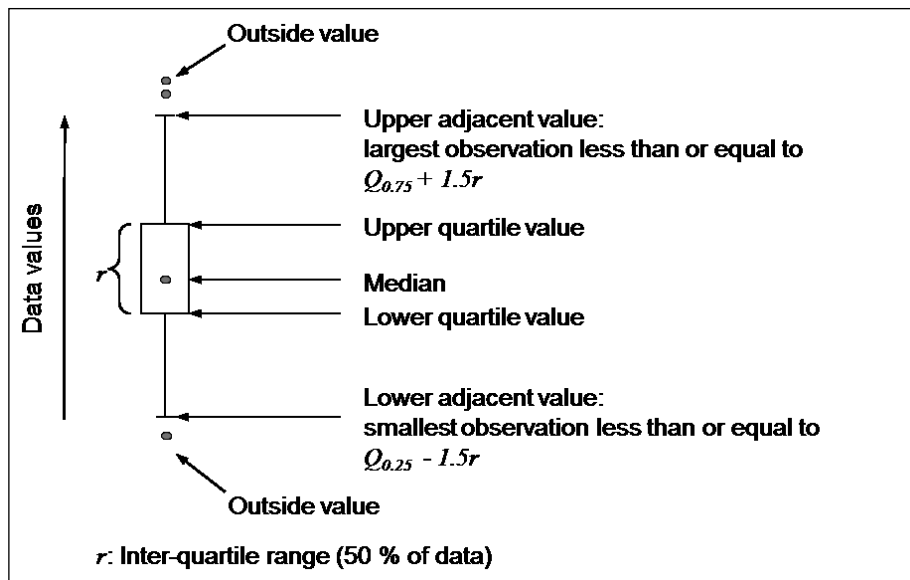


Figure 17: Tukey boxplot with the characteristics of the data set. [FABER 2012]

Interquartile range (IQR)

The difference between the upper quartile and the lower quartile is called interquartile range, where 50 % of the items of a data series are located. [FABER 2012]

$$IQR = Q_3 - Q_1$$

Coefficient of quartile deviation

The quartile coefficient of dispersion is a robust measure of spread that is used to make comparisons within and between data sets. It is computed using the first and third quartiles for each data set. The quartile deviation (QD) is therefor related to the arithmetic mean of upper and lower quartile. [ASSENMACHER 2003]

$$c_{QD} = \frac{2 \text{ QD}}{(Q_3 + Q_1)} = \frac{(Q_3 - Q_1)}{(Q_3 + Q_1)} \quad \text{with} \quad \text{QD} = \frac{IQR}{2} = \frac{Q_3 - Q_1}{2}$$

4.8 Multivariate data analysis

For all multivariate data analysis the software environment R (R-project 2008) has been used. In the following section, terms and statistical methods used for multivariate data analysis are briefly described, and details are given on methods and algorithms used.

4.8.1 Terms and methods in multivariate data analysis

Autoscaling

Autoscaled data have a mean of zero and a variance (or standard deviation) of one, thereby giving all variables an equal statistical weight. Autoscaling shifts the centroid of the data points to the origin and changes the scaling of the axes, consequently the relative distances between the data points are changed (except the original variances of all variables are equal). [VARMUZA 2009]

Mean-centering

After mean-centering, the variable has a mean of zero; the data are shifted by the mean value and the center of the data becomes the new origin – consequently the information about the origin is lost; the distances between the data points remain unchanged. Mean-centering simplifies many methods in multivariate data analysis. [VARMUZA 2009]

Variance scaling

Variance scaling standardizes each variable by its standard deviation. Usually, it is combined with mean-centering and is then called autoscaling. [VARMUZA 2009]

Principal Component Analysis

Principal Component Analysis (PCA) is a method in multivariate data analysis aiming at dimension reduction. PCA is the most frequently applied method for computing linear latent variables (components). A new coordinate system is formed by these latent variables, which is orthogonal, and where only the most informative dimensions are used.

The direction in a variable space that best preserves the relative distances between the objects is a latent variable which has maximum variance of the scores (= projected data values on the latent variable). This direction is called by definition the first principal component (PC1). It is defined by a loading vector. The corresponding scores (projection coordinates of the objects) are linear combinations of the loadings and the variables. The second principal component (PC2) is defined as an orthogonal direction to PC1 and again

possessing the maximum possible variance of the scores. In general further PCs can be computed up to the number of variables.

Latent variables from PCA optimally represent the distances between the objects in the high-dimensional variable space – at which the distance of objects is considered as an inverse similarity of the objects. Therefore, dimensions reduction by PCA is used for visualization of multivariate data by scatter plots and separation of relevant information (described by a few latent variables) from noise. PCA considers all variables thus accommodating the total data structure, and no y-data (properties) are considered. [VARMUZA 2009]

Cluster analysis

“Cluster analysis tries to identify concentrated groups (i.e. clusters) of objects, while no information about any group membership is available, and usually not even the number of clusters is known.” [VARMUZA 2009]

Multivariate calibration

Multivariate calibration can be used to model an interesting property by one or several variables if the property cannot be determined directly or only with high cost. Usually available data are split into a *training* or *calibration set* used to create the model, and a *validation* or *test set* to evaluate the performance of the model developed. Dependent on size and quality of the initial data set, different methods are available in this regard.

The application of this method is strongly dependent on how well known and how strictly defined the relationship between the variables and the interesting property is. Multivariate calibration methods are applied even if no theoretically based mathematical equations exist for the relationships between command variable and influencing parameters, and a relationship is only assumed. However, prediction performance has to be estimated very carefully, in particular for such purely empirical models. [VARMUZA 2009]

4.8.2 Algorithms and settings used in multivariate data analysis

In the following section, details on methods and algorithms used for multivariate data analysis are given, and the main algorithms and respective R-commands are presented, summarised in Table 16.

Pre-processing of data

If variables have very different origins and magnitudes, an appropriate scaling or pre-processing of the data is required [VARMUZA 2009]. Variables used for exploratory data analysis in the present thesis comprise elemental concentrations in a different dimension as well as ash content. Input data have therefore been autoscaled (cf. explanation in section 4.8.1), giving an equal statistical weight to all variables. In order to reduce the impact of potential outliers, a robust version of centering and scaling has been used, replacing the arithmetic means of the columns by the column medians, and the standard deviations of the columns by the median absolute deviations (MAD).

Principal Component Analysis

Outliers are able to artificially increase the variance in an otherwise uninformative direction which will be determined as PCA direction. However, robust estimation will determine the PCA directions in such a way that a robust measure of variance is maximized instead of the classical variance. [VARMUZA 2009] Therefore, robust algorithms were used for the PCA in order to reduce the risk of potential outliers.

Cluster analysis

In addition to visual inspection of the PCA-plots, a cluster analysis was conducted using two different methods, i.e. a partitioning method using the k-means algorithm and a hierarchical clustering method resulting in a dendrogram.

Hierarchical clustering

The relation between the objects is measured by the pairwise distances. With this method, a hierarchy of the objects is constructed according to their similarity: At the beginning each object forms its own cluster. The process is started by combining the two most similar single-object clusters in one larger cluster. In the next level the two closest clusters are merged, and so on, until finally all objects are in one single cluster. This hierarchy of similarities is usually displayed in a dendrogram. The dendrogram shows the evolution of the cluster tree from bottom to top, in the scale of the cluster distance measure. It can be used for identifying the number of clusters that is most likely inherent in the data structure. The vertical axis (height) represents the similarity between the clusters, and the horizontal axis shows the objects in a special ordering to avoid line crossing in the dendrogram. Horizontal lines indicate when clusters are combined, and their vertical position shows the cluster similarity.

The algorithm applied in the present work uses Euclidean distance as measure for similarity, and was applied to unscaled input data. Hierarchical clustering was done using the *complete linkage* method.

k-means clustering

Datamatrix X and desired number of clusters k are input data.

The most widely known algorithm for partitioning is the k-MEANS Algorithm. It uses pairwise distances between the objects, and requires the input of the desired number k of clusters. Internally, the k-means algorithm uses the so-called centroids (means) representing the centre of each cluster. For example, a centroid c of a cluster can be defined as the arithmetic mean vector of all objects of the corresponding cluster. The objective of k-means is to minimize the total within-cluster sum-of-squares.

Multivariate calibration

Multivariate calibration is done using partial least-squares regression (PLS). The optimum number of PLS components is selected via double cross-validation, searching for a low standard error of prediction (SEP) value at the least possible number of components.

For PLSR autoscaled input data were used.

Table 16: Overview about R-commands used for exploratory data analysis and multivariate calibration [R-packages].

Description	Package	Command	Remarks
Centering and/or scaling the columns of a numeric matrix.	Package base version 2.15.2	scale()	using median and mad for centering and scaling respectively
Compute a robust multivariate location and scale estimate with a high breakdown point, using the 'Fast MCD' (Minimum Covariance Determinant) estimator.	Package robustbase version 0.9-8	covMcd()	cor = TRUE for a estimate of the correlation matrix required for princomp()
Performs a principal components analysis on the given numeric data matrix.	Package stats version 2.15.2	Princomp()	covmat=C_MCD, cor=TRUE
Distance Matrix Computation	Package stats version 2.15.2	dist()	-
Hierarchical cluster analysis on a set of dissimilarities and methods for analyzing it.	Package stats version 2.15.2	hclust()	-
Perform k-means clustering on a data matrix.	Package stats version 2.15.2	kmeans()	-
Determines the optimal number of components for PLS by repeated double-CV for multivariate regression methods, like PLS and PCR.	Package chemometrics version 1.3.8	mvr_dcv()	method="simpls", selstrat="hastie", repl=50
Functions to perform partial least squares regression (PLSR)	Package pls version 2.4-3	mvr()	method="simpls", validation="CV"

5 Results and discussion

Various aspects related to the topic of slag formation in small-scale combustion units are examined. Information on properties of biomass fuels, ashes and slag samples is compiled, and ash melting and slag formation in practical combustion tests is studied. Moreover, theoretical approaches and available test methods for the assessment for ash melting properties are investigated.

An exploratory data analysis is carried out based on fuel parameters which are relevant with regard to ash melting behaviour in order to identify fuels with similar properties. Moreover, resulting groups are analysed considering fuel classes according to ÖNORM EN 14961-1, which form the basis for the interpretation of results from laboratory analyses and practical combustion tests in the following chapters.

Ash constituents of biomass fuels are analysed in order to show both characteristic composition of different biomass fuels and the typical margin of deviation. Moreover, the composition of different ash fractions is shown, and influencing factors like combustion technology, temperature and fuel composition on the release of particular elements are investigated. Ashes from laboratory furnaces and combustion processes are compared to investigate the relevance of information gained from analysing laboratory ashes with regard to real combustion appliances, and ash composition as well as ash melting characteristics are evaluated in this regard.

Based on a comprehensive set of laboratory analyses and combustion test series, both fuel related factors and technology related aspects on slag formation in small-scale combustion units are studied. In this regard ash melting characteristic as well as practical slagging behaviour of different types of biomass fuels are considered. In particular variations of wood pellets and the variety of wood pellet qualities are investigated when analysing raw-material related influencing factors on slag formation. Moreover, the effect of additives on ash melting temperatures and slagging behaviour is studied. Furthermore, different combustion technologies are compared with regard to their capability to be operated with slag forming biomass fuels. Therefore, technology related aspects in terms of grate design, ash removal technology and particular operating conditions are examined. Moreover, basic requirements are defined for combustion technologies suited for slagging fuels.

Available correlations in terms of elemental indices and empirical equations are examined using own biomass data, and their relevance with regard to ash melting properties and slag formation propensity is investigated. In addition, a new calibration model is developed. Finally, related available methods for the determination of ash melting properties are examined, aiming for developing requirements for a reliable test method to assess the slag formation tendency of solid biomass fuels.

5.1 Property related biomass classification

Biomass raw materials show considerable variations with regard to fuel properties and consequently combustion behaviour. Classification systems are available considering origin and source of solid biofuels, traded forms and particular properties such as moisture, ash content, mechanical durability or content of chlorine, nitrogen and sulphur (cf. ÖNORM EN 14961-1). A classification based on the combustion behaviour – in particular ash melting classes – would be required in order to be able to choose adequate raw materials for particular applications and combustion technologies.

In the present chapter properties of the investigated biofuels are analysed using multivariate statistical methods. Being the most important influencing parameters regarding ash melting behaviour, elemental composition and ash content are considered for evaluation. The objective of this exploratory data analysis is to group fuels showing similar properties, identify outliers within the same type of raw material and find distances and similarities between the groups. Moreover, the identified groups are considered when interpreting results in the following chapters. In this chapter, only an exploratory data analysis is conducted, more extensive calculations concerning the prediction of melting behaviour will be conducted in chapter 5.4.4, including information about ash melting and slag formation, aiming at a classification in this regard.

5.1.1 Basic information on exploratory data analysis

Due to the large number of variables, a **principal component analysis (PCA)** is conducted to enable visual inspection of the data as a whole. Moreover, two different approaches of **cluster analysis** are applied aiming at identification of similar objects and subsequent classification in this regard. Therefor a partitioning method using the k-means algorithm and a hierarchical clustering method resulting in a dendrogram are used.

All three methods are based on the same **input data**: Each object (i.e. type of fuel) is described by its ash content and the elemental composition given in oxides of the respective elements normalised to 100%. Parameters that show very low concentrations and/or are expected to have minor or no impact on the ash melting behaviour (like e.g. Ni or Pb) are removed from input data in order to reduce the number of variables. In addition to the ash content, the following compounds are considered for exploratory data analysis: Al_2O_3 , CaO , Fe_2O_3 , K_2O , MgO , Na_2O , P_2O_5 , SiO_2 . More detailed information about the calculation methods is provided in section 4.8.

5.1.2 Distances and similarities – groups of similar properties

In Figure 18 scores and loadings for the first three principal components are shown, and the symbols refer to the type of raw material. Although the plots only show part of the data structure (representing only 60 % of total variance), the main tendencies and clusters can be seen. Colours represent the classes determined via k-means algorithm which is explained below.

Visual evaluation of PC-plots

The score plot of the first two principal components shows 2 major groups: Scores of woody biomass are all located in quadrant 1 and 3, and the scores in quadrant 2 and 4 represent non-woody biomass samples.

Within the area of woody biomass a cluster is identified, in quadrant 3 close to the origin, representing mainly high-quality wood, whereas scores of low quality woody biomass are widely distributed over quadrant 1. Examining the group of non-woody biomass, an aggregation of data from cereal biomass like grain, bran, maize whole crop, corn cob and rape cake is found in quadrant 4. In quadrant 2 mainly data from lignocellulosic biomass like straw, Miscanthus and hay are located, and therein a rather dense cluster is formed mainly consisting of Miscanthus together with giant reed, particular hay samples and one straw sample. Scores of hay and straw samples are distributed over a large area.

The group of woody biomass is strongly influenced by high fractions of CaO and a low ash content, and separation into high and low quality group can generally be related to the concentrations of Al_2O_3 and Fe_2O_3 in low quality woody raw materials, which can either be related to impurities from processing (e.g. sand or soil) or other parts of the tree (e.g. bark and branches). However, the group of non-woody biomass is mainly determined by high amounts of SiO_2 and a high ash content. Moreover, cereal biomass is strongly influenced by potassium and phosphorous.

Additional consideration of PC3 allows for a further partitioning of the group of lignocellulosic biomass separating Miscanthus from hay. Also the group of cereal biomass is separated into fruit or grain parts of the plant (i.e. grain, rape cake and bran) on one hand and raw materials including straw or stalks (i.e. maize whole crop, corn cob residues and mixtures of wood with these raw materials) on the other hand.

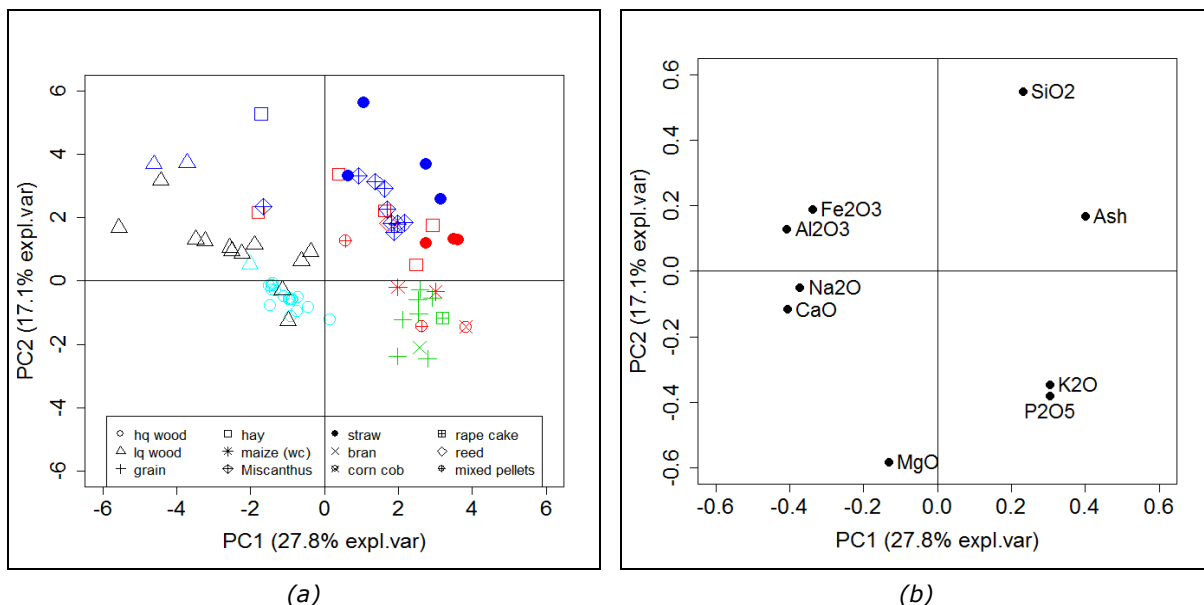


Figure 18: Scoreplot and loadingplot of PC1 vs. PC2 (a)/(b), PC1 vs. PC3 (c)/(d) and PC2 vs. PC3 (e)/(f). Assignment of scores to different groups determined via kmeans-clustering ($k=5$) is marked with different colours

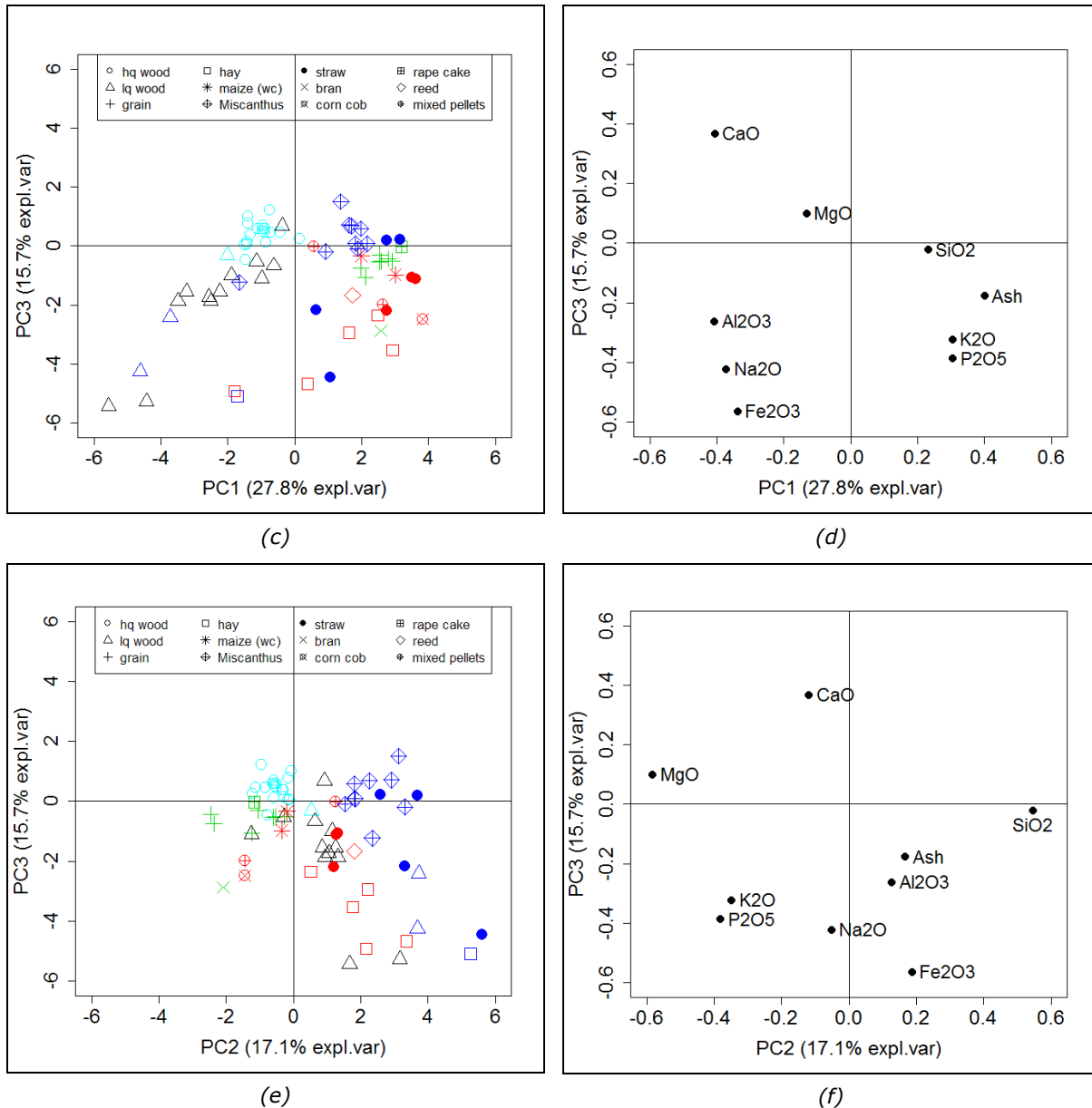


Figure 18 (continuation): Scoreplot and loadingplot of PC1 vs. PC2 (a)/(b), PC1 vs. PC3 (c)/(d) and PC2 vs. PC3 (e)/(f). Assignment of scores to different groups determined via kmeans-clustering ($k=5$) is marked with different colours

Cluster analysis

The k-means algorithm requires to predefine the number of expected or desired classes. According to the number of different types of raw materials represented by the investigated fuels, cluster analysis was done assuming both 5 and 6 major classes of biomass fuels, i.e. high quality wood, low quality wood and 3 and 4 classes for non woody biomass (e.g. different types of lignocellulosic biomass, phosphorous-rich fuels,...).

Results from k-means clustering are represented by the coloured groups in Figure 18, the dendrogram resulting from hierarchical clustering is shown in Figure 19. Similar results are found using both cluster methods. Hierarchical clustering shows three main groups

representing woody, lignocellulosic and cereal biomass. Furthermore, separate clusters are determined for low quality and high quality wood, and also sub-groups for lignocellulosic and cereal biomass are found. The “height” on the y-axis represents the distance between the respective clusters.

Using the k-means algorithm (k=5) the following groups are found (No considerable differences are found predefining either 5 or 6 classes. For k=6 group 5 is further separated into corn cob and corn cob mixed pellets):

- Group 1: High quality wood
- Group 2: Low quality wood
- Group 3: Miscanthus + straw (+ 2 LQ wood samples + 1 hay sample)
- Group 4: Grain + bran + rape cake
- Group 5: Straw + hay + maize whole crop (+ giant reed + wood/straw mix-pellets + corn cob + wood/corn cob mix-pellets)

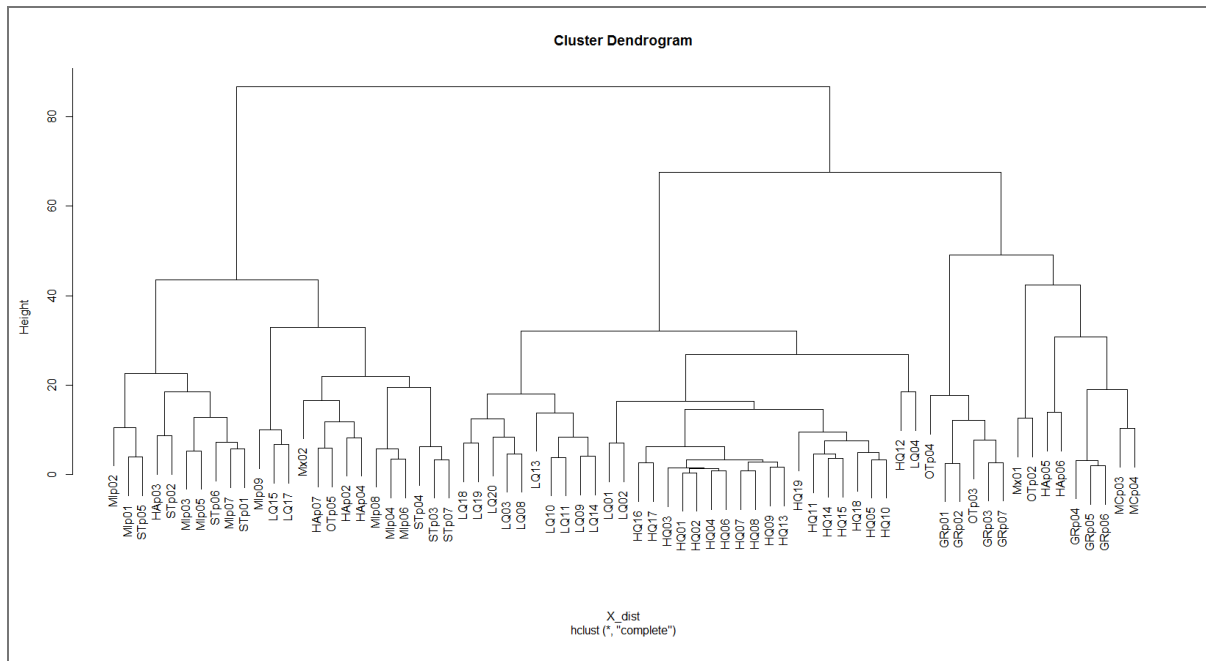


Figure 19: Dendrogram representing the distance of the investigated objects in the multi-dimensional space

Spread – range of variation of the same type of raw material

Objects representing high quality wood fuels show high similarity, and thus form a small and dense cluster. Also part of the low quality fuels are found to be close to each other, whereas other LQ wood objects are far away from this group and even show similarities to lignocellulosic samples. Thus, the unclear specification of this group comprising of all woody fuels where detailed information about the raw material source is missing, becomes apparent. Even though grain samples are found within a defined cluster, hierarchical clustering identifies sub-groups representing different types of corn (i.e. pure barley, corn, corn cob/corn cob

mix). Within the group of lignocellulosic biomass fuels a cluster is formed by *Miscanthus*, whereas objects representing hay and straw are widely distributed.

Outliers - significant differences within the same type of raw material

For raw materials represented by one or only a few samples only (e.g. bran, corn cob,...) no outliers could be determined, which is also true for straw, hay and grain: Grain samples form small sub-groups assembled to a cluster that shows no separate outliers. Due to the variations within the groups of straw and hay fuels, no cluster and consequently no outliers can be determined.

Although LQ wood pellets are found to be widely distributed as well, some remarkable samples are identified: The samples *LQ15*, *LQ17*, *LQ13* und *LQ19* (located far left in quadrant 1) show the largest distance to other LQ wood objects, and the first two of them are even assigned to the group of lignocellulosic biomass according to both cluster methods applied. On the other hand the samples *LQ01*, *LQ04* and *LQ08* are found to be close to the group of HQ wood fuels. The position of the particular samples in the cluster is in good accordance with their slag formation tendency, which is discussed more in detail in chapter 5.4.2.2. Within the HQ wood fuels no considerable outlier can be identified. The object with the largest distance to the centre of the HQ wood cluster is *HQ12*. Amongst the *Miscanthus* samples *Mip09* was found to be close to some of the LQ wood data.

5.1.3 Discussion

Comparison of classes according to EN 14961-1 and clusters determined

In ÖNORM EN 14961-1 clear classification principles for solid biofuels are provided as a basis to enable efficient trading and communication, and classification is done based on origin and source of the raw material basis. Exploratory data analysis via PCA and cluster analysis as applied in this section are to enable a classification based on measurable parameters, which is particularly relevant for fuels made of unknown raw materials, that cannot be classified according to origin and source. Moreover raw material mixtures that have to be assigned to the large group of "blends and mixtures" according to ÖNORM EN 14961-1 could be further differentiated. Table 17 shows the raw material classes according to ÖNORM EN 14961-1 assigned to particular groups determined via k-means clustering.

For HQ wood and grain samples considerable agreement is found when comparing the property related classes and the respective assignment according to ÖNORM EN 14961-1. Among the widespread cluster of woody biomass including HQ and LQ wood samples, fuels that can be assigned to *1.2.1.1* or *1.2.1.2 chemically untreated wood residues without bark* clearly stand out from whole group of woody biomass and are therefore assigned to a separate group. Also, all grain samples as well as bran and rape seed cake are grouped in one cluster.

Wide analogy was also found for the group of grasses (whole plant) as well as grasses (blends and mixtures). All *Miscanthus* samples were found in one cluster (group 3) and only the single giant reed-sample was assigned to another group (group 5). The reason for the similar properties within this class is probably that from the large group of grasses only *Miscanthus*

samples are analysed. Also the major part of hay samples are grouped in one cluster (group 5), with only one sample being attached to a different group.

Table 17: Classes according to ÖNORM EN 14961-1 assigned to the groups determined via k-means clustering.

Group according to k-means clustering	Raw material classes according to ÖNORM EN 14961-1 represented in the respective group
1	1.2.1.1 Chemically untreated wood residues without bark , deciduous 1.2.1.2 Chemically untreated wood residues without bark , coniferous 1.2.1.4 Chemically untreated wood residues with bark, coniferous
2	1.2.1.4 Chemically untreated wood residues with bark, coniferous 1.4 Blends and mixtures (woody biomass)
3	1.4 Blends and mixtures (woody biomass) 2.1.1.2 Straw parts (from cereal crops) 2.1.2.1 Whole plant (of grasses) 2.1.2.5 Blends and mixtures (of grasses)
4	2.1.1.3 Grain (from cereal crops) 2.1.1.4 Husks and shells (from cereal crops) 2.2.1.2 Oil seed crops (from chemically untreated herbaceous residues)
5	2.1.1.1 Whole plant (from cereal crops) 2.1.1.2 Straw parts (from cereal crops) 2.1.2.5 Blends and mixtures (of grasses) 2.1.2.1 Whole plant (of grasses) 4.1 Blends (of different types of biomass)

Distribution among two groups is observed for LQ wood fuels and straw. Usually, high variability is attributed to the properties of straw, leading to a differentiation of this fuel class. All wood pellets where no information about source and origin of the raw material is available are summarised under the term LQ wood fuels corresponding to class *1.4 Blends and mixtures (of woody biomass)* according to ÖNORM EN 14961-1. This group consists of a broad variety of fuels, probably containing both products made of almost bark-free stem wood and used wood or logging residues. Thereby the distribution among different clusters can be explained. However, only one sample is attached to the cluster of HQ wood fuels.

Above all, it has to be mentioned that no fuel class according to ÖNORM EN 14961-1 is distributed over more than 2 groups determined via cluster analysis.

Applicability and potential of this method

A classification based on fuel properties facilitates the assessment of fuels made of unknown raw materials. Moreover, raw material mixtures being very inhomogeneous with regard to fuel properties or raw materials showing a broad variety in this regard can be characterised.

The classification is based on parameters that are relevant with regard to ash melting properties. Therefore, the classes defined by this method shall represent groups with different ash melting properties, and ideally particular groups can be related to particular ash melting properties or a defined slag formation tendency. In general it was found that fuels usually showing considerable slag formation are rather assigned to groups 4 and 5, whereas reduced

slag formation tendency is usually observed for the fuels in classes 1, 2 and 3. Investigations regarding the correlation of ash melting properties and practical slag formation tendency to the groups determined can be found in another section (cf. section 5.4).

However, elemental analyses are required which are in general expensive and also time consuming. A problematic aspect regarding the applicability of the method is that results of both PCA and cluster analysis vary dependent on the whole data set, i.e. the investigated sample itself has an impact on the cluster formation. In order to use this method for a standardised assessment, this problem may be resolved by providing a vast set of basic data where the investigated sample is assigned to.

5.2 Variability of ash composition and elemental release

Elemental composition is one of the most decisive factors with regard to slag formation of biomass ashes. Therefore, knowledge about typical compositions of raw materials is required. Moreover, information about the elemental transfer from fuel to ash and the influence of combustion conditions may be important in this regard. Another aspect is the variability of different ash fractions and the influence of the sampling position on ash composition.

In the following chapter, typical concentrations of the main ash forming elements as well as their variation range are presented for the investigated fuel ashes. Different ash fractions and slag samples are analysed, and the elemental transfer from fuel to ash during the combustion process is studied.

5.2.1 Ash composition of different fuels

In general the ash composition is very similar to the composition of inorganic matter in the particular fuel, regarding non-volatile elements which usually represent the major ash fraction. In Figure 20 the composition of the main inorganic compounds in 3 different fuel samples (i.e. woody biomass, grain and herbaceous biomass) and the respective ashes are compared. It is obvious that the ash composition is basically determined by the composition of the particular fuel. Apart from inhomogeneity of the fuel, variations are mainly due to different ash reactions and resulting integration or release of particular compounds, which will be discussed more into detail in chapter 5.2.3 and 5.2.4.

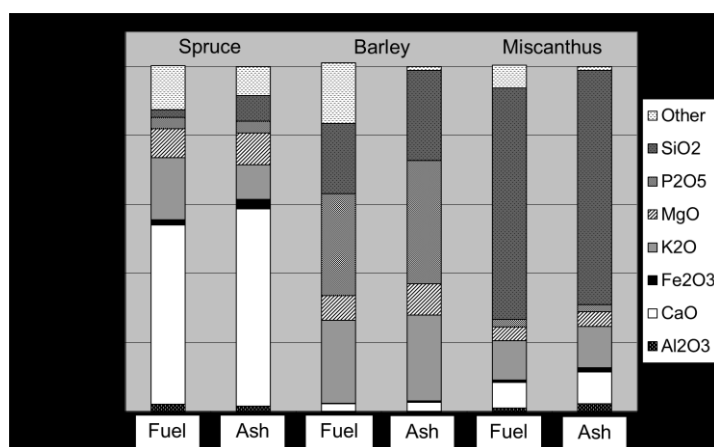


Figure 20: Comparison of major ash forming elements in fuel and bottom ash for spruce (bark-free), barley and Miscanthus.

Composition and properties of biomass fuels vary significantly, and consequently this also applies for biomass ashes. On a general level, basic characteristics of the ash composition can be attributed to different fuel classes, which is also confirmed by the results in chapter 5.1: Ash from woody biomass e.g. shows high contents of Ca whereas herbaceous biomass is rich in Si. Increased fractions of P but also K and Si can be found in grain. However, considerable variations are found within these classes, and even among different samples of the same type of raw material. An overview about the typical composition and the variability of different biomass ashes is given in Table 18. The respective values for the main constituents, i.e. CaO, K₂O, P₂O₅ and SiO₂, are shown in Figure 21.

Table 18: Variation of the ash composition – Average value (median) and spread (coefficient of quartile deviation C_{QD}) for the main constituents in bottom ash samples of different biomass fuels.

Type of fuel		Al ₂ O ₃	CaO	Cl	Fe ₂ O ₃	K ₂ O	MgO	P ₂ O ₅	SO ₃	SiO ₂
		Fraction in %								
HQ wood n=10	Median	1.6	54	0.03	2.3	14	9.5	3.5	1.2	6
	Spread (C_{QD}) in %	32	5	28	37	11	12	26	20	27
LQ wood n=7	Median	7.4	36	0.02	4.0	10	6.3	1.7	1.0	27
	Spread (C_{QD}) in %	37	25	69	19	12	21	36	32	30
Maize whole crop n=3	Median	1.5	9	0.30	1.6	24	9.0	18.4	1.4	35
	Spread (C_{QD}) in %	24	16	64	27	10	4	5	48	7
Straw n=3	Median	1.0	8	0.24	0.8	27	2.7	2.3	1.1	56
	Spread (C_{QD}) in %	70	17	87	47	19	8	21	39	9
Grain n=5	Median	0.3	4	0.01	0.4	25	9.1	35.4	0.3	24
	Spread (C_{QD}) in %	54	33	71	14	5	5	4	78	52
Miscanthus n=8	Median	0.9	8	0.04	1.6	16	4.2	2.3	0.4	66
	Spread (C_{QD}) in %	55	10	27	33	25	20	45	32	7
Hay n=6	Median	5.9	15	0.31	2.4	20	4.4	6.0	1.4	43
	Spread (C_{QD}) in %	23	23	48	14	29	9	26	24	12

Characteristic composition of different fuel classes

The main fraction of ash from woody biomass consists of CaO, whereas ash from herbaceous biomass is dominated by SiO₂ and K₂O. In addition P₂O₅ plays a major role for biomass containing considerable fractions of grain. The fraction of Fe₂O₃ is below 5 % in most biomass ashes and increased values are only found in ashes from low quality wood, most probably due to the presence of bark in the raw material basis. Concentrations of Al₂O₃ in the ash are below 4 % for most fuels. Values up to 10 % can only be observed for low quality wood, hay and particular straw samples, and may either be attributed to the presence of bark in woody biomass or mineral impurities. The concentration of MgO is generally low – in particular for herbaceous biomass – ranging from 2 % – 6 %. Increased values of 10 % – 15 % MgO are found for ashes from woody biomass and fuels containing grain (i.e. energy grain and maize whole crop). The fractions of both Cl and SO₃ are comparably low, and rather relevant as to the formation of particulate emissions, deposit formation or corrosion reactions than ash melting behaviour.

Range of variation

For CaO strong variations can be observed for low quality wood which can be attributed to varying fractions of bark in the fuel. Relative variations are also high for non-woody biomass fuels due to the low absolute value. Strong variations for K₂O within the same fuel class are found for herbaceous biomass i.e. straw, Miscanthus and hay. This may be explained by the faster metabolism of annual crops – in particular in the herbaceous plant material – compared to wood and consequently the increased influence of external factors like e.g. soil quality or fertilising. The fraction of P₂O₅ shows only little variation for the investigated P-rich fuels i.e.

energy grain and maize whole crop as well as for woody or herbaceous biomass, where absolute concentrations in general are very low. Considerable variations for SiO_2 are found for most fuels except HQ wood and maize whole crop, and relative variation is particularly high for grain and also woody biofuels, where absolute concentrations are significantly lower than in herbaceous biomass. Si concentration in wood is mainly influenced either by bark addition or soil contamination of the raw material. Variations in grain are most probably due to species or cultivar. Variations of Fe_2O_3 and Al_2O_3 are strong when considered as relative values but fractions of these compounds are generally low. For MgO no significant tendency was found.

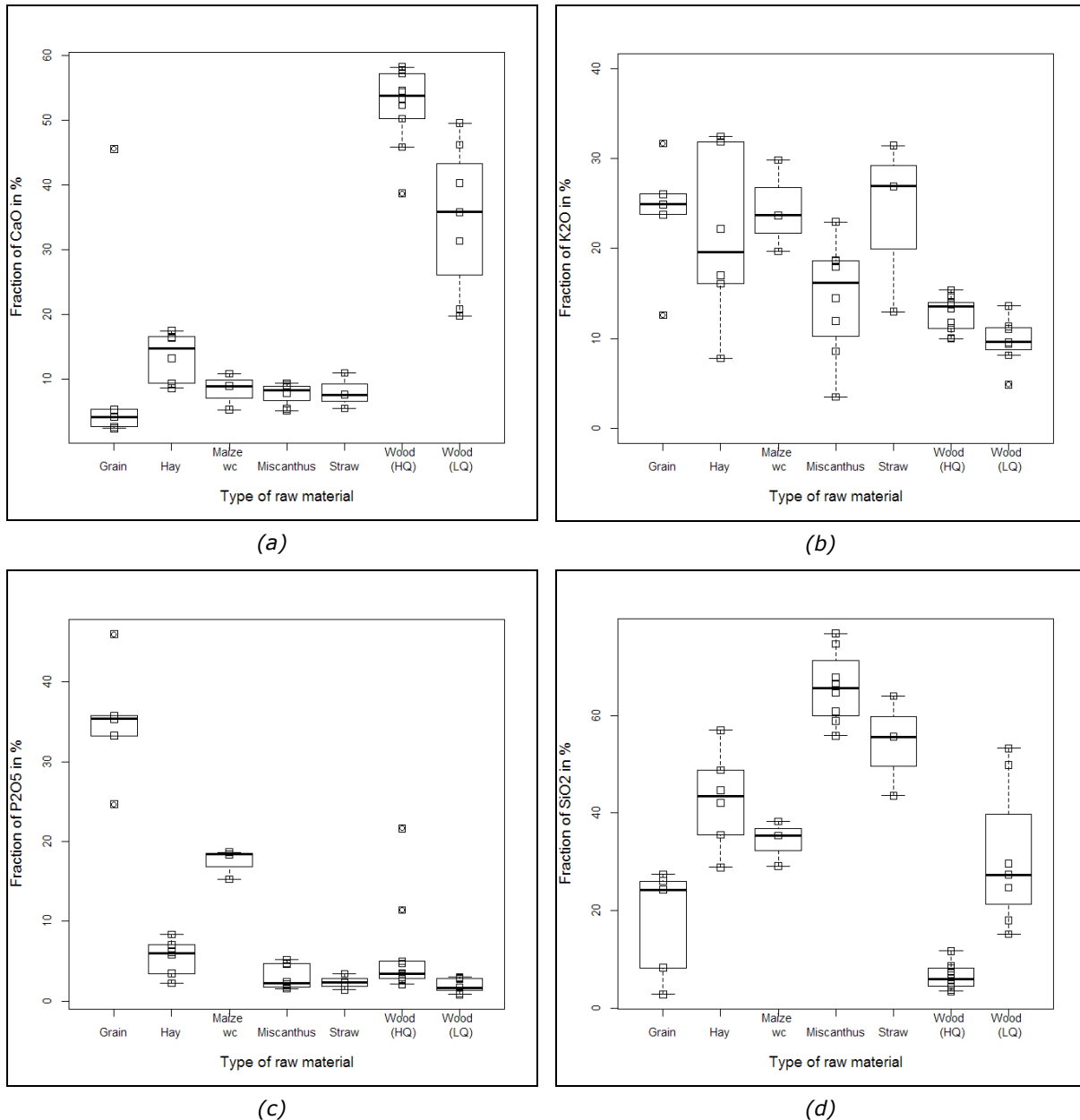


Figure 21: Variability of the fraction of CaO (a), K_2O (b), P_2O_5 (c) and SiO_2 (d) in the fuel ash shown for different types of fuels.

5.2.2 Variation among ash fractions and sampling positions

In general, the major part of the ash accumulates as *grate ash* or *bottom ash* in the combustion zone in small scale combustion units. Smaller amounts of ash are carried to the rear part of the boiler – usually the heat exchanger section. In Figure 22 the composition of bottom ash and ash from the heat exchanger of different types of woody (a) and non-woody biomass (b) are shown.

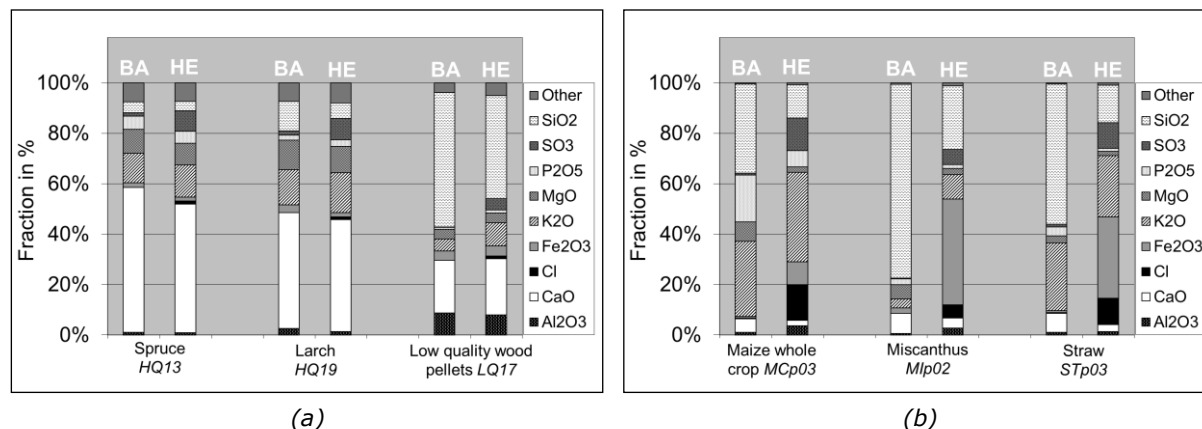


Figure 22: Composition of bottom ash (BA) and ash from the heat exchanger (HE) from the combustion of wood pellets (a) and pellets of non-wood biomass (b).

Similar to findings from large combustion units (cf. section 3.3.3), the fraction of elements forming volatile compounds is increased in the ash samples collected in the heat exchanger section, whereas the share of other compounds is constant or even reduced: For all HE-ashes, a significant increase of the content of Cl and S and slightly increased concentrations of K can be observed. On the other hand concentrations of Si, Mg and Ca are reduced when compared to the bottom ash composition. No differences can be observed for the fraction of Fe in ashes from the combustion of wood pellets. In contrast, the Fe-content in HE-ashes from the combustion of non-woody biomass is strongly increased. This high amount could originate from boiler material being corroded by reactions with S- or Cl-components of the flue gas.

Related to the increased amounts of Cl, S and K in the ash from the heat exchanger part of the boiler, a depletion of the respective elements is assumed for the bottom ash. Therefore, lower concentrations of these elements are expected in the bottom ash from combustion experiments than in ashes produced under laboratory conditions. This has to be taken into account when evaluating fuels based on the composition of laboratory ashes, but also when defining sampling procedures.

Elemental composition of ash and slag particles

In Figure 23 ash and slag composition from the combustion of three different fuels are compared. Increased amounts of silicon are found in slag material, and also aluminium is slightly increased. Concentrations of calcium and potassium are constant or slightly reduced proportionally to the strong increase of silicon (cf. low quality wood pellets LQ03 in Figure 23).

The increased content of silicon can be explained by enrichment during the melting process due to a eutectic composition or varying reactivity of different ash compounds formed during combustion.

Figure 23: Composition of ash (Ash) and slag (SL) from the combustion zone from the combustion of wood pellets with bark, low quality wood pellets and pellets made of maize (whole crop)



5.2.3 Influence of combustion conditions on the bottom ash composition

Ash composition can vary dependent on combustion conditions in terms of e.g. combustion temperature, residence time and gas atmosphere (cf. section 3.3.3). In the following section the variation range of various ash forming elements is investigated. Oxide concentrations of the main ash constituents i.e. Al, Ca, K, Mg, P and Si are investigated. In addition Na is shown due to its potential effect on the melting properties of an ash mixture. Moreover, S, Cl and Zn are presented because of their relevance for corrosion reactions and the formation of deposits and particulate emissions. In Figure 24 (a)-(j) bottom ash (including slag) from one fuel sample fired in different combustion units are compared for selected woody and non-woody biomass.

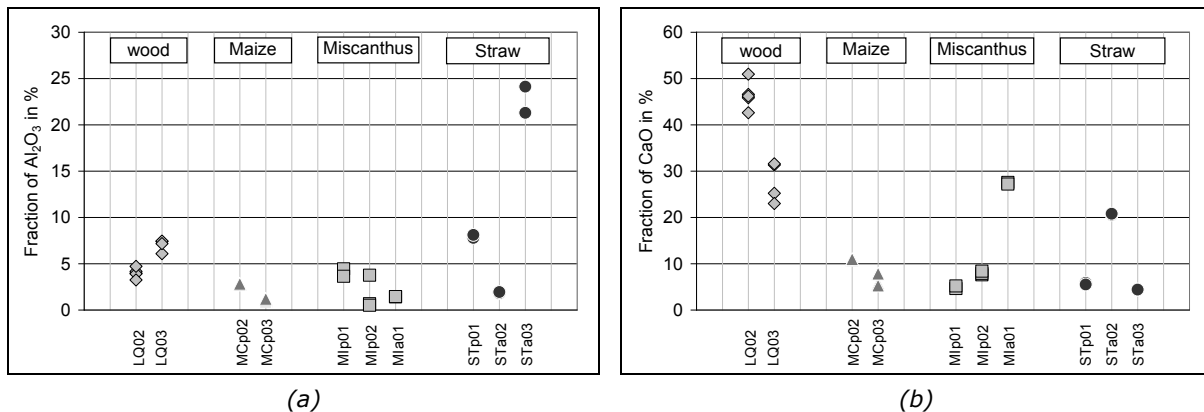


Figure 24: Variation of oxide fractions in ashes from one fuel sample fired in different combustion units for samples of wood, maize whole crop, Miscanthus and straw. Each fuel is presented in one row.

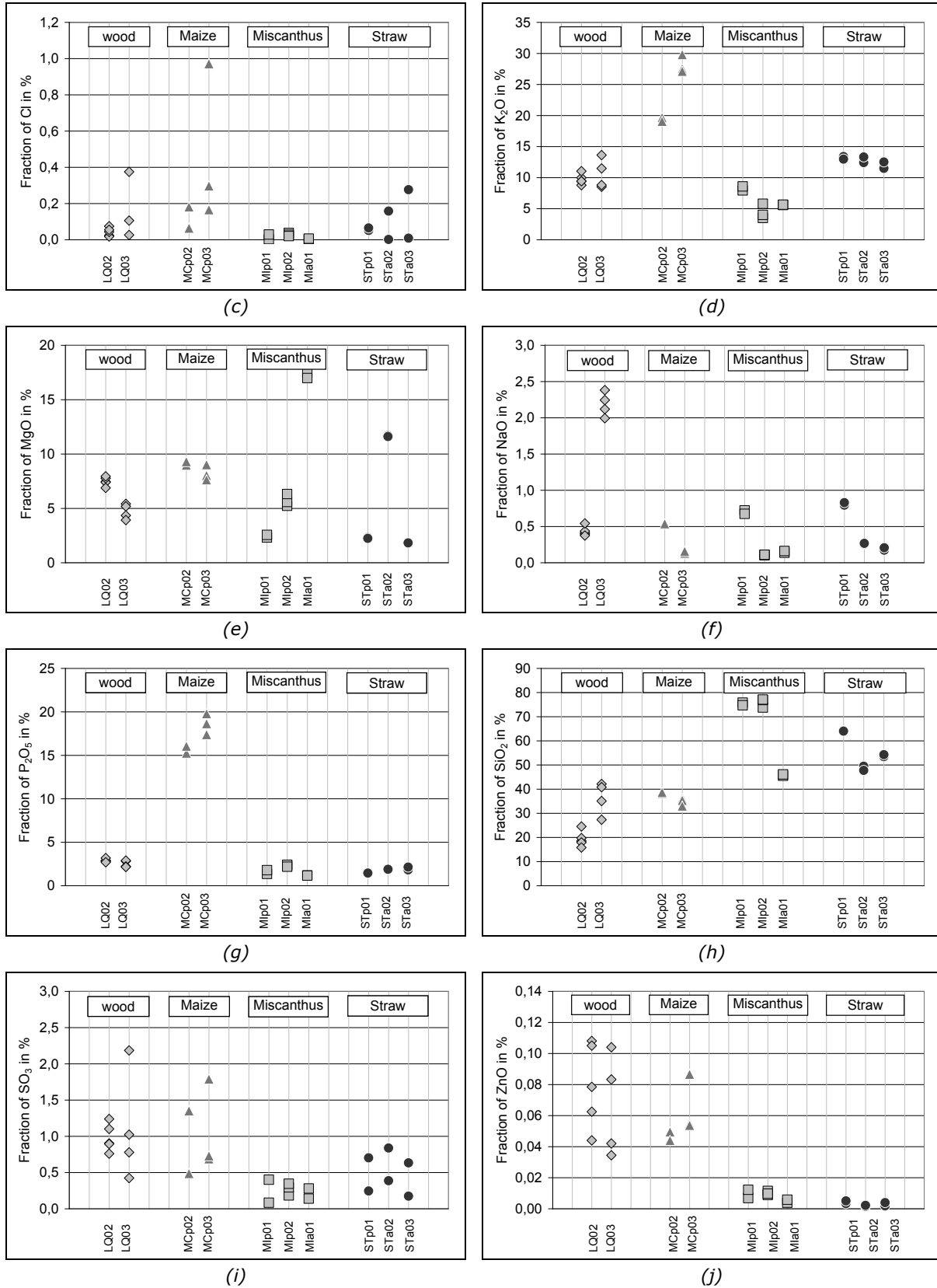


Figure 24 (continuation): Variation of oxide fractions in ashes from one fuel sample fired in different combustion units for samples of wood, maize whole crop, Miscanthus and straw.

As expected, the concentrations for CaO and SiO₂ are nearly constant, showing only little variations for the ashes from the combustion of wood. Also small fluctuations are observed for the concentration of Al₂O₃, MgO and P₂O₅, in the combustion ashes. However, strong variations are observed for the fractions of Cl, SO₃ and ZnO.

In order to compare the variation of particular ash compounds, the coefficient of quartile deviation (C_{QD}) is determined as a relative and robust measure of spread. Separate values are calculated for each fuel sample based on the composition of different ashes from the combustion of this fuel, and results are summarised in Figure 25.

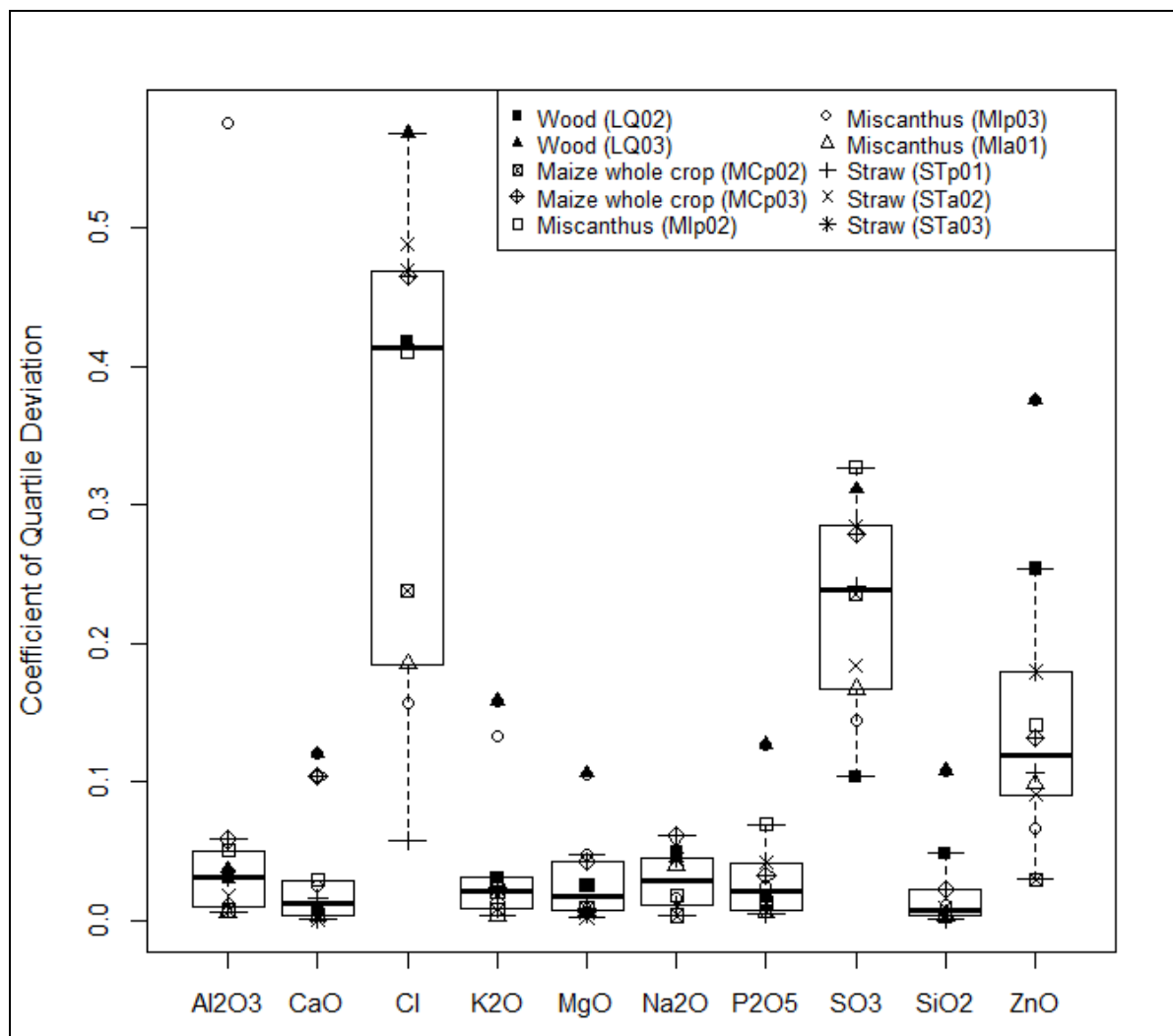


Figure 25: Variation of oxide fraction in combustion ashes. (Each data point is calculated from different ashes (fired in different combustion units) of the same fuel).

Considerable variations are found for Cl, SO₃ and ZnO with about 20 % – 50 %, 15 % – 30 % and 10 % – 20 % respectively. However, elemental concentrations in ashes from the same fuel show similar results for all other investigated elements, independent from the prevailing combustion conditions. Variations for these elements are usually around 3 %.

Even though the influence of temperature on the release of the alkaline metals K and Na has previously been documented (cf. section 3.3.3), this influence seems to be less relevant than

fuel-type and -composition respectively at usual combustion temperatures. For S, Cl and Zn high release rates can be expected above a certain temperature (700 °C–800 °C for Cl, 800 °C–1000 °C for S and 850 °C for Zn – cf. 3.3.3 Release of ash forming elements). Although usual temperatures in the combustion zone are even higher, strong variations of the concentrations of these elements can be observed. Generally, the release of sulphur varies significantly, also depending on the type of sulphur compounds (organic or inorganic). Besides the combustion temperature also the particle size of the fuel, residence time and access of air may have an influence in this regard. Moreover, slag formation can lead to areas with lower temperatures or different air ratios, and thus influence the ash composition.

However, taking into account the percentage of each constituent in addition to its variation range, bottom ashes with a similar composition can be expected from the same fuel burnt in different combustion appliances: The highly varying components Cl, SO₃ and ZnO together only represent 0.1 % – 2.7 % of total ash for the investigated ashes, considering both woody and non-woody fuels. Consequently, ashes from the combustion of the same type of raw material do not show considerable variations regarding their basic composition. However, variations of the highly volatile compounds need to be considered with regard to the formation of emissions or deposits.

Release of Cl, K, S and Zn from bottom ash of different fuels in boilers L6 and L7

Combustion conditions in terms of temperature, residence time, agitation of the fuel bed or gas-chemistry in the combustion zone vary dependent on the combustion technology. Considerable variations were found for Cl, S and Zn in bottom ashes from the same fuel. In the following section, ashes from the same fuel are compared for particular combustion technologies, focusing on these elements. Moreover, the release of K is investigated because of its inclination to form volatile compounds during combustion (e.g. KCl). Figure 26 shows the remaining fractions of Cl, S and Zn in ashes from the combustion of different types of non-woody biomass in unit L6 and unit L7.

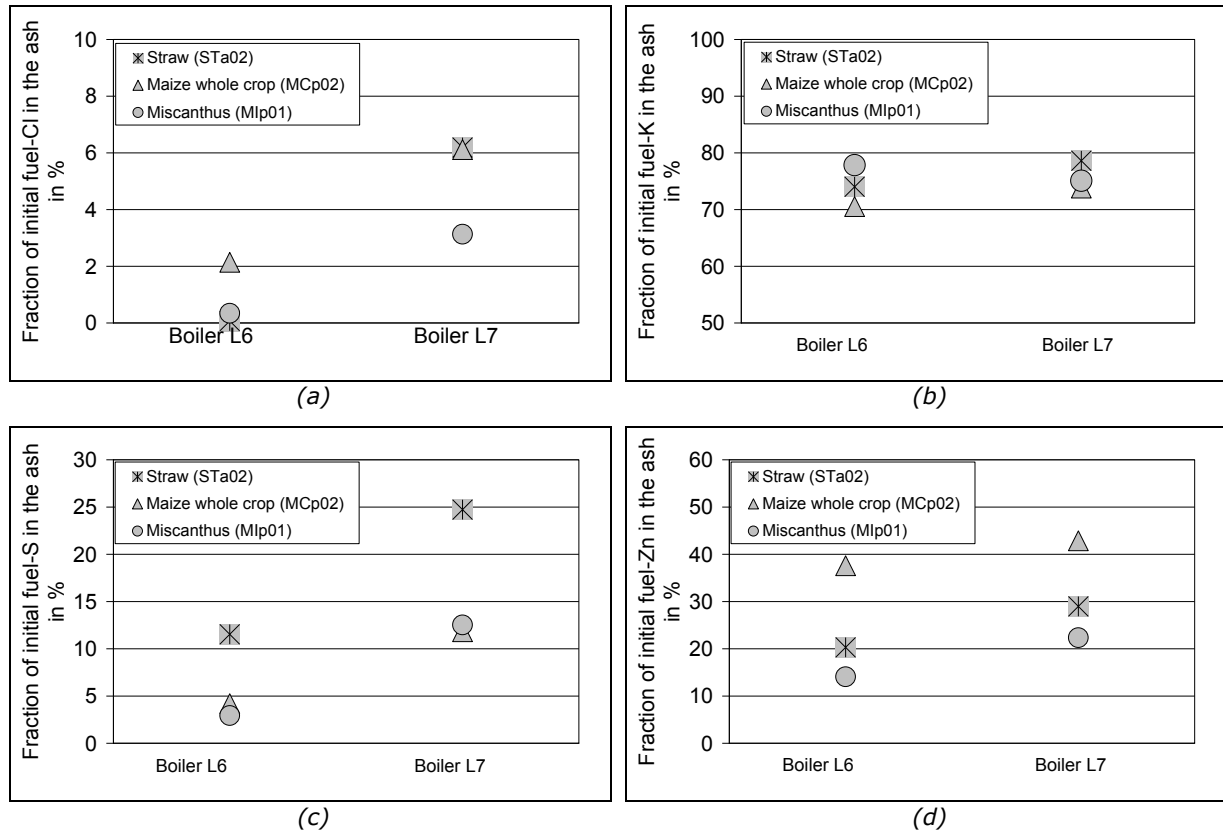


Figure 26: Residual fraction of chlorine (a), potassium (b), sulphur (c) and zinc (d) in the ash from the combustion in two different small-scale combustion units

Increased fractions of S, Cl and Zn are found in the ashes from boiler L7 compared to boiler L6. In spite of very little remaining amounts, differences by factor 3 for both Cl and S, and of about 1.5 for Zn are determined, and similar trends are found for different types of fuels. However, for K only small variations can be observed.

Boiler L6 is a pellet stove where the ash is removed in discrete intervals by manual grate cleaning. Thus, residual ash in general remains on the grate for a long period of time, and fuel and residual ash are not stirred until the ash is removed. Boiler L7 is a underfeed burner where the ash is transported over a burner plate and removed continuously at the edge of the plate, pushed by the successive fuel. Thus, the residence time in the combustion zone is limited, and combustion residues are continuously agitated until the ash is discharged. Lower fractions of the investigated elements in the ashes of boiler L6 may be attributed to the longer residence time in the combustion zone. However, the influence of additional parameters like e.g. temperature or atmosphere could not be quantified.

Comparison of bottom ash samples from different combustion units

In Figure 27 elemental fractions are shown for ashes from the combustion of wood pellets with 2 % bark (LQ02) in 4 different combustion units (i.e. L1, L3, L4 and L5). All boilers were operated at standard settings except boiler L4 where the air ratio in the primary combustion zone was reduced. Moreover, an additional ash sample was considered from unit L3 operated with reduced primary air supply.

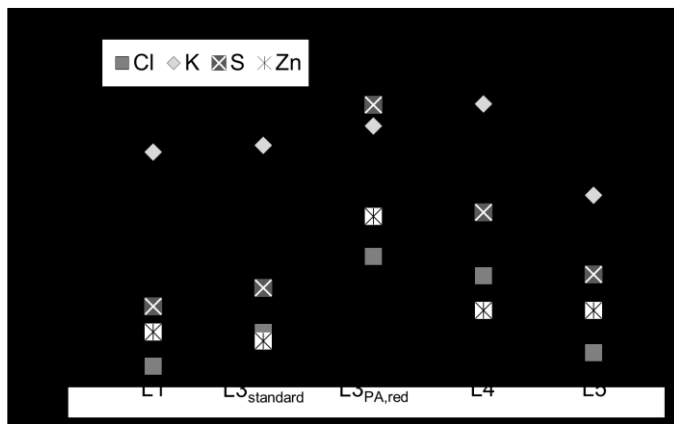


Figure 27: Residual fractions of chlorine, potassium, sulphur and zinc in ashes from the combustion of wood pellets with 2 % bark (LQ02) in different combustion units.

Similar tendencies are observed for S and Cl, showing the lowest retention in boiler L1 and the highest concentrations for ashes from boiler L3 operated with reduced primary air supply (*PLred*). Values differ from about 20 % to almost 100 % for S and from 2 % to about 40 % for Cl respectively. Even for K considerable variations are observed ranging from 60 % in unit L5 to 95 % in boiler L4. The highest concentration for residual Zn was also found in the ash of unit L3 when operated with reduced primary air supply. However, only minor differences are found for Zn in all other ashes, ranging from 10 % to 20 % without showing a clear tendency.

Low retention rates for volatile ash compounds in boiler L1 can be attributed to the high residence time of the ash in the combustion zone: The grate in boiler L1 is designed as a burner pot where the major part of the ash remains and is only removed in discrete intervals.

A significant effect of reduced air supply in the primary combustion zone is evident as highest concentrations of the investigated elements are found in ashes from boiler L4 and boiler L3_{PLred}. Both boilers were operated with reduced primary air supply, and consequently lower temperatures and a reducing atmosphere in the primary combustion zone is assumed. Moreover, reduced particle-gas contact due to lower air supply may have an influence. However, the influence of temperature or atmosphere could not be quantified.

In Table 19 the total composition of the investigated bottom ashes is shown: Similar fractions of the particular compounds can be found in all ashes. Variations of major constituents like e.g. SiO₂ or Fe₂O₃ considerably influence the relative share of all compounds. However, being related to the Ca-concentration the release factor is not affected. As explicated above the highly varying components Cl, SO₃ and ZnO are of minor relevance with regard to total ash composition.

Table 19: Composition of bottom ashes from the combustion of low quality wood pellets with 2 % bark (LQ02) in different combustion units.

	Bottom ash boiler L1	Bottom ash boiler L3 _{standard}	Bottom ash boiler L3 _{PLred}	Bottom ash boiler L4	Bottom ash boiler L5
Al ₂ O ₃ in %	4.0	4.7	4.4	3.6	3.2
CaO in %	46.6	42.6	42.2	45.1	50.9
Cl in %	0.0	0.1	0.2	0.2	0.0
Fe ₂ O ₃ in %	4.8	3.7	4.2	2.8	2.7
K ₂ O in %	10.0	9.4	10.1	11.8	8.8
MgO in %	7.5	6.9	6.8	7.5	7.9
MnO ₂ in %	4.6	3.9	3.9	5.3	5.6
Na ₂ O in %	0.4	0.5	0.5	0.6	0.4
P ₂ O ₅ in %	2.9	2.7	2.8	4.8	3.2
SO ₃ in %	0.8	0.9	3.2	1.8	1.2
SiO ₂ in %	18.5	24.5	21.5	16.7	15.8
ZnO in %	0.1	0.0	0.2	0.1	0.1

5.2.4 Influence of fuel composition on elemental release

The release of particular elements and compounds is clearly influenced by combustion conditions. Moreover, the ash composition as a whole can have an impact on elemental concentrations with some elements forming especially stable or rather volatile compounds. In the following section, the release of highly volatile elements is investigated with regard to different fuel classes.

Chlorine, potassium, sulphur and zinc have been identified as the elements showing the strongest variations with regard to ash composition. In Figure 28 residual fractions of these elements in the combustion ashes from woody and non-woody biomass are shown for different fuel classes determined from the cluster analysis in chapter 5.1, and only fuels without additives are considered. Data shown in this figure are obtained from different combustion units. Nevertheless, a comparison seems acceptable since each unit was used for fuels representing different fuel classes. Moreover, differences found dependent on the fuel composition are more significant than variations due to combustion conditions for the same fuel.

In general, the fraction of initial fuel-chlorine that remains in the fuel ash is relatively low, and the share of residual Cl is clearly below 10 % for most ashes. Increased values are observed for some LQ wood samples in fuel class 2 and particular samples in class 5, i.e. maize whole crop and straw. However, only 4 samples exceed the fraction of 20 %. Both low residual fractions of about 10 % as well as sporadically strong variations are also reported from literature (cf. section 3.3.3).

Residual potassium in fuel ashes is found from about 50 % up to more than 90 %, and the range of variation is considerably large for all classes with a margin of about 30 %. Values

found for group 1 (HQ wood) are lower when compared to other fuel groups, amounting to 60 % – 70 % for most samples. For other fuels in average 80 % of the initial fuel potassium remain in the combustion ash. Maximum values in this regard are found for *Miscanthus* ashes in class 3, and slightly lower values are only found for class 5 representing samples of maize whole crop, hay and straw. Basically, these results are in accordance with findings regarding the elemental influence on potassium release as reported in literature (cf. section 3.3.3). However, no distinct correlation to particular elemental concentrations (e.g. Si) or factors (e.g. Si-(Ca+Mg+Cl) [GILBE 2008 (1)]) could be verified for the dataset investigated. Only a certain trend was found, showing lower release rates for potassium in the range of 50 % – 80 % for fuels with a Si-content of below 200 mg/kg, and values of 70 % – 90 % for fuels with higher Si fractions.

The major part of sulphur is released during combustion, and only minor fractions remain in the bottom ash: About 10 % are remaining after the combustion of *Miscanthus* and LQ wood samples assigned to fuel class 3, and hardly any residual sulphur is found in the combustion residues of energy grain represented by class 4. About 20 % of the initial fuel sulphur and a considerable variation range of about 30 % are found for ashes from fuels assigned to fuel class 5. In ashes from the combustion of HQ wood and LQ wood, represented by class 1 and class 2, about 20 % and 20 % – 40 % respectively of the initial fuel sulphur remain. This is in good accordance with findings from literature (cf. section 3.3.3), showing similar release rates and stating potentially increased release rates for Si-rich fuels (KNUDSEN 2004).

Strong variations between the fuel classes are observed for the retention of zinc in the fuel ash: An average fraction of 20 % can be found in ashes from biomass assigned to class 1, 2 and 3, i.e. woody biomass (HQ and LQ) and *Miscanthus*. For class 4 and 5 representing grain, straw, maize whole crop and hay increased fractions of 40 % – 80 % of the initial zinc in the ash are determined. A certain relationship to the initial concentration of zinc in the fuel can be found: For fuel-zinc concentrations up to 20 mg/kg the major part is released during combustion, and a maximum of 30 % (in general below 20 %) remains in the ash. For fuels showing increased zinc concentrations, strong variations of remaining fractions up to 90 % are observed. Whereas similar results for the release of Zn from wood ash are found in literature (cf. section 3.3.3), no reference values for non-woody fuels were found.

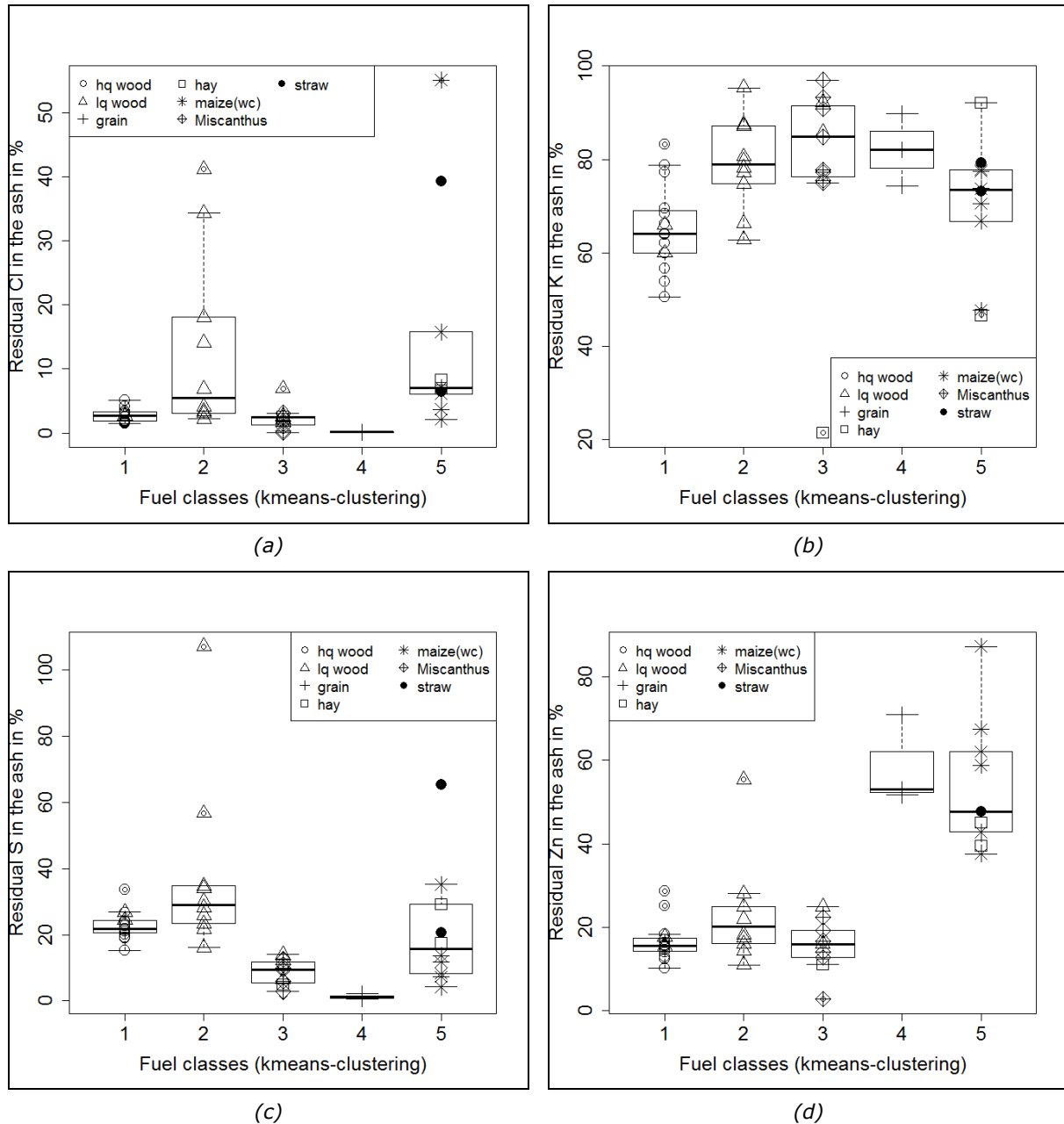


Figure 28: Residual fractions of chlorine (a), potassium (b), sulphur (c) and zinc (d) in the bottom ash of different combustion units for different fuel classes determined via cluster analysis. (Woody and non-woody biofuels without additives are considered.)

5.2.5 Discussion

The composition of biomass ashes is generally determined by the composition of the fuel used, and basic characteristics of the ash composition can be attributed to different fuel classes. Considerable variations regarding the elemental composition are particularly found for non-woody biomass fuels, but also for woody biomass containing different raw materials like bark, logging residues or even waste wood apart from bark-free stem wood. Among samples from the same type of raw material, most significant differences are found for the Si-

content, showing variations of about 50 % for grain fuels, and the concentration of K, with a variation range of 20 % – 30 % for straw, Miscanthus or hay.

Increased concentrations of Si and also Al were found in **slag particles** when compared to **residual bottom ash**, indicating that some compounds or mixtures are more reactive and therefore preferably form slag while other ash fractions only react at higher temperatures. Consequently the melting characteristics of the ash composition as a whole does not necessarily provide sufficient information to predict slag formation tendency in real combustion appliances. Similar results were found in ÖHMAN 2004 (1) or GILBE 2008 (2).

Significant differences were found comparing the composition of **bottom ash** and **heat exchanger ash** of a boiler, showing increased values for S, Cl and K, similar to findings from larger combustion appliances (cf. section 3.3.4).

Regarding the **release of particular elements**, in general good accordance with previous findings from literature was obtained. However, certain characteristics were identified that may be attributed to the real combustion conditions in contrast to laboratory tests that form the basis for most literature data. Moreover, additional information for non-woody fuels was gained: About 10 % of the initial fuel-chlorine were found to remain in most bottom ashes, but also strong variations regarding the Cl-release were observed. With about 60 % – 90 % the main fraction of fuel-potassium was found to remain in the ash, which is high when compared to reference values from laboratory tests, but in good accordance with available information from real combustion application (cf. section 3.3.3). Release rates for S of 70 % to almost 100 % are in good accordance with previous research results, whereat values for non-woody biomass fuels are rather high (cf. section 3.3.3). Release rates of 80 % for Zn from woody biomass fuels are in good accordance with previous findings. However, for a considerable number of non-woody biomass samples lower release fractions of 20 % – 60 % were determined, and no reference values are available in this regard.

Considerable **variations due to combustion conditions** are only found for Cl, S and Zn. Variation ranges amount to 20 % – 50 % for Cl, 15 % – 30 % for S and 10 % – 20 % for Zn for ashes from the combustion of the same fuel sample in different appliances or with varying combustion conditions respectively. Regarding the release of all three elements, similar trends are found for particular combustion units, and even K shows a comparable tendency. The most significant effect was observed for variations regarding primary air supply, resulting in changes regarding the gaseous atmosphere and possibly also reduced temperatures. However, the impact of particular parameters could not be quantified.

No major impact of the above described effects on the basic bottom ash composition is expected, and bottom ashes with a similar composition will occur from the same fuel burnt in different combustion appliances: The highly varying components Cl, SO₃ and ZnO together only represent 0.1 % – 2.7 % of total ash for the investigated ashes, considering both woody and non-woody fuels. Consequently, ashes from the combustion of the same type of raw material do not show considerable variations regarding their basic composition. Moreover, these elements are of minor relevance for ash melting reactions (cf. section 3.3.2). However,

variations of the highly volatile compounds need to be considered regarding the formation of emissions or deposits.

Significant **influence of the ash composition** on the release of particular elements was shown. Whereas only little variations were observed for the release of K dependent on combustion conditions, considerable differences were found between the fuel groups (derived from cluster analysis in section 5.1): The lowest values for residual K in the fuel ash were determined for group 1 (i.e. HQ wood) with 60 % – 70 %, and maximum values were found for Miscanthus mainly in the range of 80 % to almost 100 %. This is in good accordance with literature data, stating increased release rates for Ca-rich fuels, and stronger integration in Al- and especially Si-rich ashes (cf. section 3.3.3). Large differences were also determined for residual Zn with low fractions of about 20 % for wood and Miscanthus (group 1, 2 and 3) and considerably higher fractions of about 50 % and above for grain, straw, hay and maize w.c. (group 4 and 5). The results for woody biomass are therefore in good accordance with previous findings (cf. section 3.3.3), however values for non-woody biomass have not been reported yet.

Residual fractions of Cl considerably vary within group 2 (LQ wood fuels) and group 5 (straw, hay, maize wc). However, apart from that characteristic, no influencing factors on the Cl-release could be identified. Slightly reduced release rates for S were shown for woody compared to non-woody biomass: Considerable fractions only remain in woody biomass (group 1 and 2) and particular samples of maize w.c., hay and straw assigned to class 5.

5.3 Comparing laboratory ashes and ashes from combustion processes

Several laboratory tests or analyses are conducted using laboratory ashes. These ashes are generally prepared under standardised procedures in laboratory furnaces in order to receive reproducible and comparable results. Therefore, the fuel is ground to small particles, and a homogeneous sample is used. In laboratory furnaces, slow and defined heating rates are applied. The residence time in the combustion zone is significantly longer and temperatures are relatively low compared to real combustion appliances. Moreover, no mechanical stresses e.g. by ash removal devices act on the ash.

In a real combustion process, fuels and ashes are exposed to variable conditions with regard to temperature, residence time and gas atmosphere, dependent on the operating conditions and the technology used. These parameters as well as size and properties of the fuel particles can influence the release of particular elements from the fuel ash: Some compounds which are present in the laboratory ash can be released when exposed to higher temperatures during the combustion process. On the other hand, longer residence times and small fuel particles in a laboratory oven may facilitate the release of elements that remain in the ash after a short exposure time in a combustion unit. Thus, differences regarding the ash composition between laboratory ashes and combustion ashes are expected. In Table 20 the main differences regarding the combustion conditions in a laboratory oven and in a combustion unit are summarised.

Table 20: Comparison of combustion conditions during ashing in a laboratory oven and in typical combustion appliances.

	Laboratory oven	Combustion appliance
Fuel	Homogeneous sample ground to small pieces	Larger fuel particles, pellets often show a kind of sealed surface
Heating rate/ temperature	Slow and defined heating rates, low maximum temperatures (e.g. 550 °C according to ÖNORM EN 14775)	Usually fast temperature rise after ignition, Maximum temperatures exceeding 1000 °C.
Atmosphere	Defined / constant atmosphere	Varying conditions (oxidising/reducing)
Residence time	Several hours (≥ 4 hours according to ÖNORM EN 14775)	Varying considerably dependent on combustion technology
Mechanical stresses	No agitation or (forced) transport	Agitation of the fuel bed e.g. by successive fuel or by tools used for ash discharge.

In the present chapter differences between ashes from laboratory furnaces and combustion processes are investigated. Therefore, ash composition and ash melting characteristics of laboratory ashes and ashes from combustion appliances are compared and evaluated.

5.3.1 Elemental composition of laboratory ashes and ashes from combustion appliances

According to DIN 51719 a temperature of 815 °C is used for the production of laboratory ashes. In compliance with the actual European standard (ÖNORM EN 14775) ash samples are

only exposed to 550 °C for this purpose. For a comparison of laboratory ashes and ashes from combustion units, both methods have been applied to a set of wood pellets. Moreover, ash samples from combustion tests with woody and non-woody biomass have been studied.

Release of carbon – unburnt material and carbonate in the fuel

During the combustion process, ash forming elements in the fuel react with oxygen in the combustion air forming mainly salts and oxides. The bigger part of carbon in the fuel is released as CO₂, whereas some carbon remains as unburnt mainly carbon containing organic material or bound as carbonate in the ash.

In Figure 29 the sum of oxides is shown for laboratory ashes (at both temperatures) and ashes from different combustion appliances, calculated from the composition of major and minor ash forming elements. For the laboratory ashes the fraction received from c, h, and n is additionally presented.

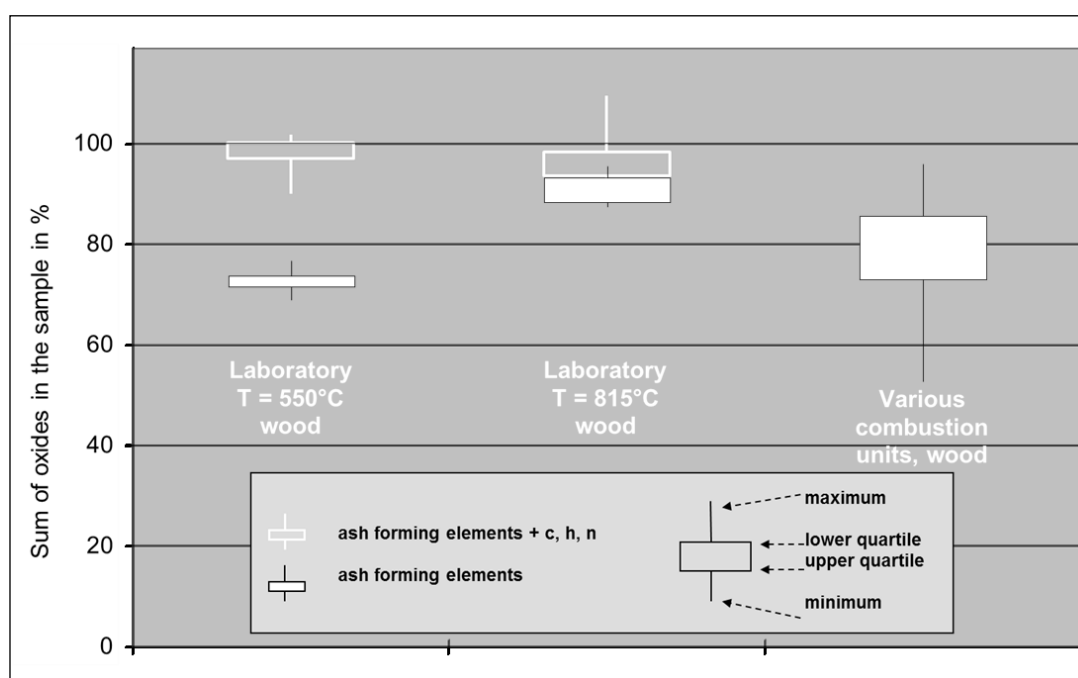


Figure 29: Sum of oxides in samples of laboratory ashes at different temperatures (550 °C and 815 °C) and ashes from combustion tests in different types of boilers.

It can be seen that about 100 % of the sample can be identified when considering carbon as carbonate, and it can be assumed, that the main part of residual carbon is bound in inorganic ash constituents. Nitrogen and hydrogen are of minor relevance due to their low concentrations.

A comparison of the laboratory ashes shows that there is still a considerable fraction of carbon in the ash at 550 °C; whereas at 815 °C about 90 % of the sample consists of salts and oxides from so called ash forming elements. Consequently, also the ash content is higher for 550 °C ashes.

Results of ashes from combustion units show stronger variations due to the varying conditions in the respective appliances. In most ashes less carbonate is found than in 550 °C-laboratory

ashes. Though higher temperatures can be assumed in the combustion chamber of the boilers, a higher percentage of carbon compounds is found when compared to laboratory ashes at 815 °C. This can be explained with larger fuel particles and comparably short residence times in real combustion, impeding the release of fuel-carbon.

Concentration of ash forming elements

The elemental composition of ashes and the respective fuels is of particular importance for combustion relevant properties like corrosion potential, ash melting properties and the formation of deposits and particulate emissions.

In Figure 30 concentrations of particular ash constituents in different wood pellet ashes from the combustion in a muffle furnace at 550 °C and 815 °C (laboratory ashes) and from the combustion in one combustion unit (unit L1) are compared. Typical variations due to combustion conditions as determined in chapter 5.2.3 are marked for the ashes from real application.

Regarding the concentration of CaO, MgO, SiO₂, Al₂O₃ and P₂O₅ no significant differences can be found between laboratory ashes and ashes from combustion units. Lower concentrations of SO₃, Cl, ZnO, Na₂O and K₂O are found in ashes from boilers when compared to 550 °C laboratory ashes, but the extent of reduction varies dependent on the particular fuel.

Differences are also found between the 550 °C and 815 °C laboratory ashes: Results for chlorine are significantly lower in 815 °C laboratory ashes and even below the values for combustion ashes, although temperatures in a combustion unit can be assumed to be above that temperature. A reason for this could be the longer residence time and smaller particles in the laboratory procedure. ZnO concentrations for 815 °C ashes are found to be lower than in 550 °C ashes, and slightly above the values determined for ashes from combustion units, which is in good compliance with the temperature gradient assumed. In general concentrations of Na₂O and K₂O in 815 °C ashes are lower than in 550 °C ashes, and variations are most probably due to the elemental composition of the fuel.

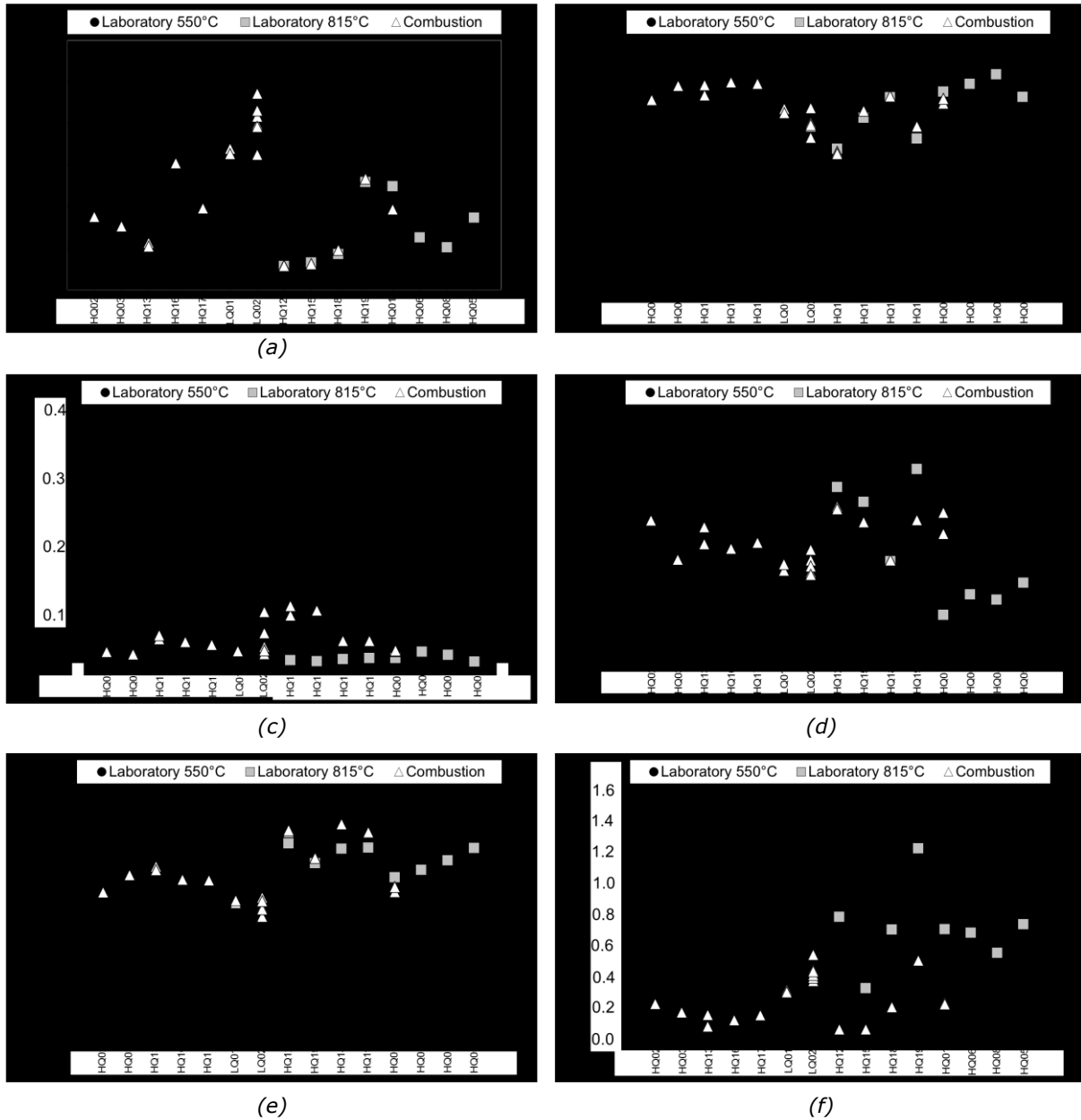


Figure 30 (Part 1): Fraction of ash forming oxides in laboratory ashes and ashes from combustion appliances burning wood pellets. Variation range for combustion ashes is marked as determined in chapter 5.2.3.

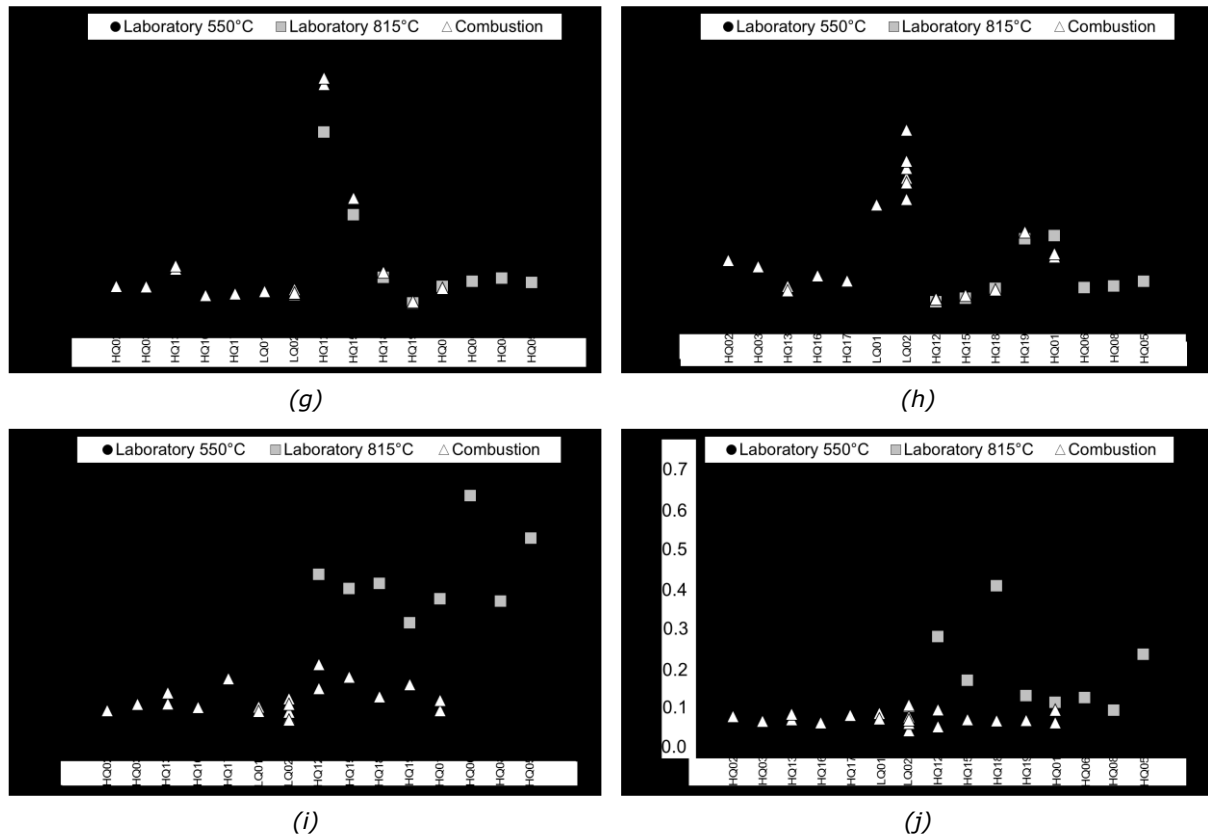


Figure 30 (Part 2): Fraction of ash forming oxides in laboratory ashes and ashes from combustion appliances burning wood pellets. Variation range for combustion ashes is marked as determined in chapter 5.2.3.

For the elements showing the strongest variations, i.e. Cl, K, S and Zn, fractions in the ash related to the initial concentration of the respective element are presented in Figure 31 (due to its negligible occurrence in plant material Na is not considered here).

For chlorine a distinct influence of temperature can be shown: Only a small fraction of the initial amount of chlorine – below 5% – is found in the laboratory ashes produced at 815 °C and in ashes from combustion appliances where temperatures of around 1000 °C can be assumed. In 550 °C laboratory ashes residual concentrations are significantly higher with about 15% - 20% for most samples, and an increased variation can be observed. These results are in good accordance with findings from the investigation of laboratory ashes of wood fuels (cf. FRANDSEN 2005, VAN LITH 2008).

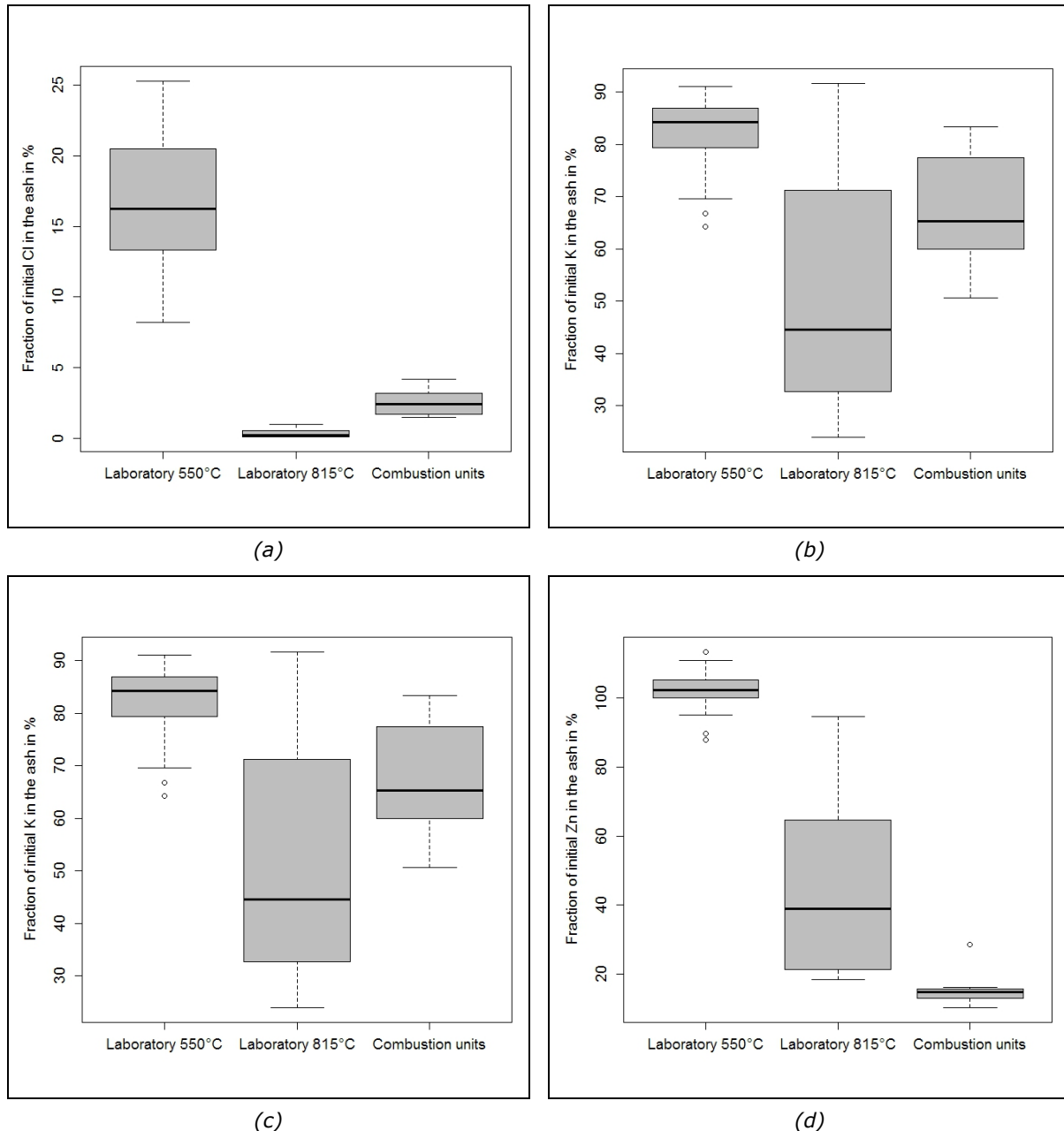


Figure 31: Remaining fractions of chlorine (a), potassium (b), sulphur (c) and zinc (d) in the ash from wood pellets combustion for laboratory ashes (550 °C and 815 °C) and ashes from combustion appliances.

For potassium a certain influence of the combustion temperature can be observed as well. In 550 °C laboratory ashes about 70 % – 90 % of the initial fuel-K are found, whereas values for 815 °C laboratory ashes are in general between 30 % and 70 % and even below. Ashes from real combustion processes are found in between: Remaining elemental fractions are significantly lower than in 550 °C laboratory ashes, which can be explained by the difference in combustion temperatures. However, concentrations in the ash are high when compared to 815 °C laboratory ashes. Although temperatures in the combustion unit can be assumed to be higher than in the muffle furnace this might be due to lower residence times. Similar

differences can be observed when comparing findings from literature, showing much higher release rates from ashes in laboratory tests compared to ashes from real combustion applications (cf. section 3.3.3).

Only about 20 % of the fuel-sulphur remain in the ash from combustion units. The respective values are considerably higher for both laboratory ashes: About 40 % – 70 % and 60 % – 80 % of sulphur are found in 550 °C and 815 °C ashes respectively. Good accordance with reference values is found for boiler ashes, and also the tendency of lower release rates at lower temperatures was found. However, remaining fractions in laboratory ashes are high when compared to literature data for woody biomass fuels (cf. section 3.3.3). Differences between the two laboratory ashes are most probably within the variation range, also considering the relatively low values for initial fuel-S.

A clear temperature dependence can be shown for the concentration of zinc in different ashes: Virtually all Zn from the fuel is found in 550 °C laboratory ashes. Strong variations are found for 815 °C laboratory ashes showing a residual fraction of 20 % – 90 % of Zn in the ash. In boiler ashes only 10 % – 30 % of the initial amount of Zn can be found, which is in good accordance with previous findings from literature (FRANDSEN 2007, VAN LITH 2008).

5.3.2 Ash melting behaviour of laboratory ashes and ashes from combustion appliances

Usually, characteristic temperatures of the ash fusion test are used for an evaluation of the ash melting properties of solid biomass fuels. Results from laboratory ashes and ashes from combustion units are evaluated in order to investigate the comparability in this regard. Therefore, tests have been conducted using both, ashes produced according to ÖNORM EN 14775 and ash samples from combustion appliances. In Figure 32 softening temperature (SOT) and flow temperature (FT) of laboratory and boiler ashes are compared for both ashes from woody and non-woody biomass. The continuous line shows the ideal progression for temperature of boiler ash is equal to laboratory ash. In addition the reproducibility limit of 50 °C according to DIN 51719 is marked with dashed lines.

For the softening temperature (SOT) results from laboratory ashes and ashes from combustion units differ a lot. Better correlation is found for the flow temperatures (FT) of laboratory and boiler ashes. However, for some types of biomass large differences determined for any characteristic temperature. In general, values from wood and *Miscanthus* samples are in good accordance whereas laboratory ashes from straw, grain and in particular maize show large deviations when compared to the respective boiler ash.

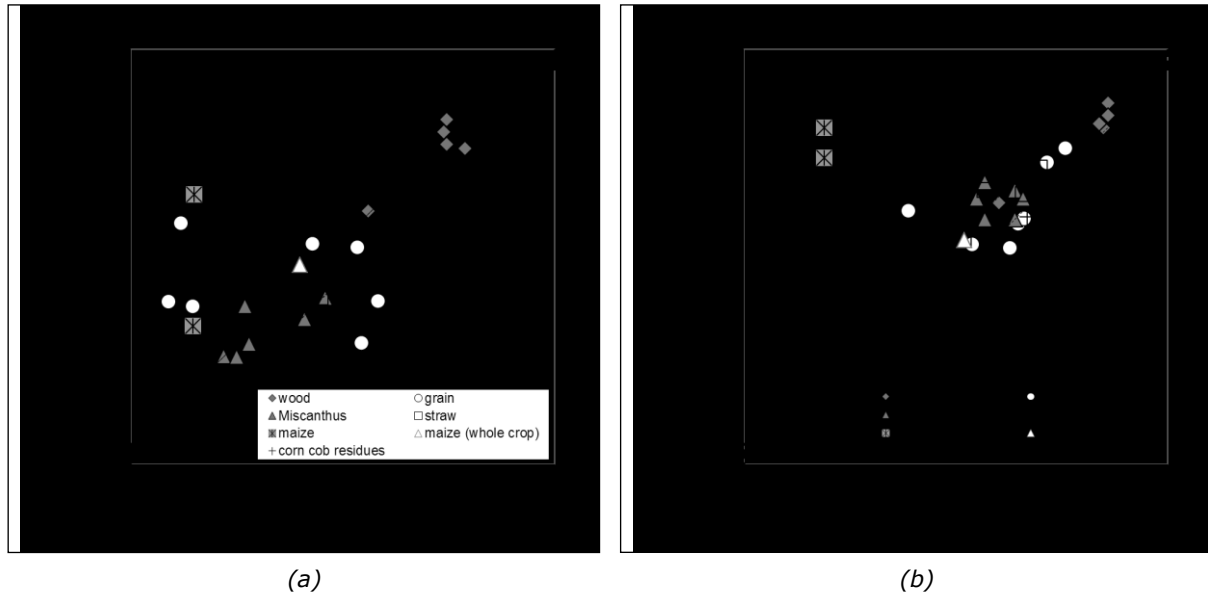


Figure 32: Softening temperature (a) and flow temperature (b) for laboratory and boiler ashes from the combustion of woody and non-woody biomass. Accordance of values (continuous line) and limit of reproducibility (dashed line) are shown in addition.

Inspecting the investigated data via PCA shows that the samples showing large deviations are all found in an area that represents high fractions of phosphorous, potassium and also silicon. No influence of the use of additives on the quality and performance of the analysis was found.

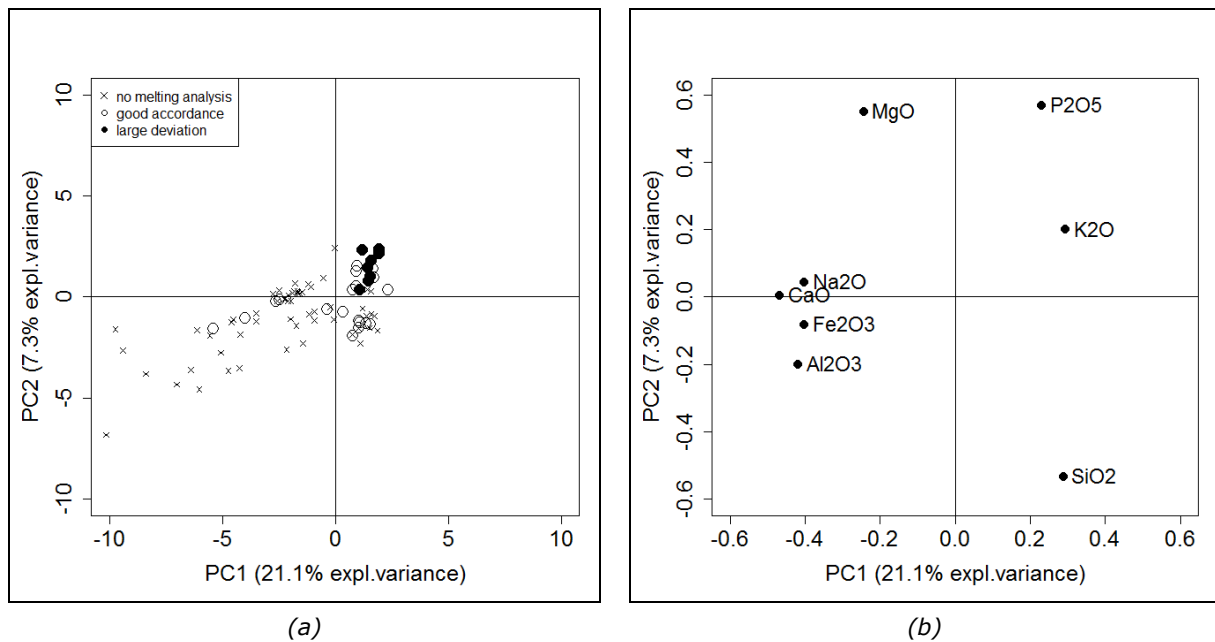


Figure 33: Scoreplot (a) and loadingplot (b) of the first two principal components (main ash forming elements are considered as parameters, both fuel samples with and without additives are included)

5.3.3 Discussion

For most ash forming elements, the variations due to different combustion conditions are more significant than differences between laboratory and ashes from combustion appliances. Results from boiler ashes and laboratory ashes produced at 815 °C are similar for the most part, and considerable deviations are only found for laboratory ashes produced at 550 °C regarding the concentrations of Cl, K, Na, S and Zn. Regarding the assessment of ash melting properties, only K is considered as relevant as Cl, S and Zn are only present in very low concentrations, and furthermore minor influence on ash melting reactions is attributed to these elements (neglecting Na which is typically not a relevant element in biomass fuels).

Evaluating the elemental release during combustion based on knowledge gained from 550 °C-ashes, release rates would be estimated too low: Up to 3 times as much sulfur, 5-7 times as much chlorine and about the tenfold amount of Zn remain in the low-temperature laboratory ashes when compared to the respective boiler ashes.

Variations observed are mainly attributed to different combustion temperatures. However, regarding the results for the release of Cl and particularly K, it seems likely that also the residence time has a relevant impact on the release of particular compounds: Although temperatures in the combustion zone are probably higher than 815 °C, higher fractions of potassium remain in the boiler ashes. In addition to temperature and residence time, also a certain impact of the fuel composition could be assumed. However, only minor relevance is attributed to that aspect since only woody biofuels with a similar basic composition have been considered for the present evaluation.

Comparing the characteristic melting temperatures determined for laboratory ashes and the respective combustion ashes, good accordance is found for typically low-slagging fuels like e.g. wood or *Miscanthus*. On the contrary, large differences are observed for fuels that are generally showing low ash melting temperatures and a high practical slag formation tendency. However, no direction or trend can be identified for these deviations as both higher and lower temperatures are found for combustion ashes when compared to laboratory ashes. Similar differences that were previously observed for coal ashes were related to the loss of potassium and reactions between mineral residues at higher temperatures experienced by ashes in combustion appliances[WALL 1998].

Furthermore, scores of the particular samples in the PCA plot suggest that considerable deviations are mostly probable for fuels rich in P, K and Si.

5.4 Fuel related influencing factors on ash melting and slag formation

Some biomass fuels are considered as problematic concerning their ash melting properties and slag formation propensity, which is particularly relevant for non-woody raw materials. In this regard e.g. straw or grain are linked to severe slagging more than other non-woody biomass fuels like e.g. Miscanthus, but the sole knowledge of the raw material type is not sufficient to predict the slagging properties of a biomass fuel.

Among woody biomass fuels, slagging problems are often attributed to certain raw materials like hardwood, larch and wood fractions containing bark, roots or branches. Moreover, non-mineral additives – usually starch-containing substances – are sometimes considered to be relevant, and also soil contamination of the raw material is important in this regard. Fuel properties that are often linked to slagging fuels are a large fraction of fines, dark colour or high ash content.

The use of mineral additives like e.g. lime to improve the ash melting properties is frequently discussed – in particular for non-woody biomass fuels (cf. section 3.3.5). Another measure is the optimization of fuel properties by mixing different raw materials. However, only little information on the combustion performance of mixed biomass pellets is available.

In the present chapter various fuel related aspects are examined regarding their influence on slag formation and ash melting. Different raw materials are compared, and also the variability within one type of fuel is investigated. In this regard a special focus is set on the variation and improvement of wood pellets. Assessing the relevance of particular fuel properties, the impact of elemental composition as well as ash content is investigated. Moreover, the relevance of ash melting temperatures with regard to slag formation under real combustion conditions is studied, and the effect of additives is examined.

Investigations aim at evaluating the significance of fuel properties or parameters with regard to ash melting behaviour, and to identify the most suitable parameters for assessing the ash melting properties of solid biomass. Moreover, it is analysed if the utilisation of additives or the mixing of raw materials is reasonable for and improvement of the ash melting properties.

5.4.1 Ash melting and slag formation of different types of biomass

Various fuels were analysed with regard to characteristic ash melting temperatures. Moreover, several fuels were tested in state-of-the-art small-scale combustion systems in order to evaluate the slag formation tendency. Combustion tests were conducted in different boiler technologies under well-controlled conditions, and the slagging behaviour was assessed qualitatively after an experimental duration of 24h. (In some cases, experiments had to be stopped earlier due to severe slag formation or overloaded ash box.) A quantitative assessment of the slag formed from the combustion of different types of biomass in one type of boiler was done by sieving the combustion residues.

Characteristic melting temperatures of different biomass raw materials

Ash melting analyses of the 550 °C laboratory ashes have been performed for a number of different fuel samples. Table 21 provides an overview about typical values for characteristic

melting temperatures, as well as their variation range. In Figure 34 results for softening temperature (SOT) and flow temperature (FT) are shown for different raw materials, and the variation range is investigated considering the different fuel classes identified in chapter 5.1.

Table 21: Variation range of characteristic softening temperature (SOT) and flow temperature (FT) for different biomass fuels (without additive).

		SOT _{MIN} in °C	SOT _{MAX} in °C	Δ_{SOT} in °C	FT _{MIN} in °C	FT _{MAX} in °C	Δ_{FT} in °C
HQ wood	n=19	1340	1500	160	1390	1560	170
LQ wood	n=16	930	1420	490	1203	1460	257
Miscanthus	n=8	820	1172	352	1150	1260	110
Hay	n=6	820	1150	330	1180	1320	140
Straw	n=7	726	840	114	1022	1084	62
Maize w.c.	n=2	910	1000	90	990	1120	130
Grain	n=7	747	1185	438	790	1360	570

Highest temperatures for both SOT and FT are measured for wood fuels, in particular HQ wood samples, whereas lowest values are clearly found for straw, and furthermore for grain (regarding SOT) and maize whole crop (regarding FT). The variability of SOT is either similar and in many cases considerably stronger than for FT, and narrow ranges for both SOT and FT are found for HQ wood, straw and maize whole crop (being only represented by 2 samples however).

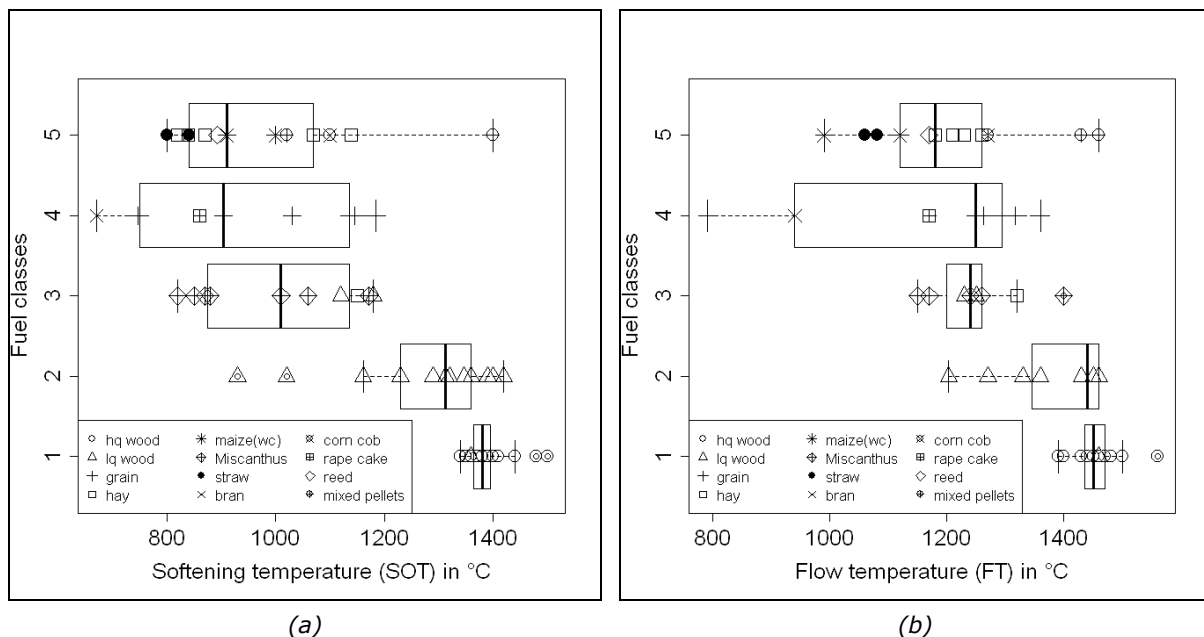


Figure 34: Variation range of softening temperature (SOT) (a) and flow temperature (FT) (b) for different types of biomass.

Both SOT- and FT-values are found in a narrow range for HQ wood samples (fuel group 1) at around 1370 °C and 1450 °C respectively. Group 2 only includes LQ wood fuels, and shows significantly lower values for both characteristic temperatures when compared to the HQ wood samples in group 1. Group 3, 4 and 5 are more heterogeneous, comprising of different types

of biomass each. However, for a number of fuels considerable variations are even found within the same fuel type. Values from different *Miscanthus* samples e.g. in group 3 cover a wide range with softening temperatures from 820 °C up to 1172 °C, whereas hay and LQ wood assigned to group 3 are found in the upper field for both SOT and FT. The strongest variations and at the same time the lowest values are found for group 4 comprising grain and related biomass like wheat bran and rape cake. Within group 5 low melting temperatures are found for straw and maize whole crop, and also some hay samples show SOT-values below 900 °C. In the upper range of group 5 softening temperatures of more than 1000 °C are measured for corn cob residues, hay and mixed pellets. Flow temperatures show similar tendencies with highest values of more than 1400 °C for mixed pellets made of wood and straw as well as wood and corn cob residues.

Slag formation tendency in practical combustion tests

In Table 22, a **qualitative assessment** of the slag formation for different fuel samples and combustion units is shown. In spite of varying fuel properties and combustion conditions a general tendency for slag formation can be observed for the particular fuel classes. In all combustion units, reference experiments were conducted with HQ wood pellets, and no slag formation could be observed. The *Miscanthus* samples showed a different behaviour: No or only little slag formation was found after combustion of sample MIp02, whereas for MIp01 considerable slag formation could be observed in both combustion units investigated. Straw caused severe or considerable slagging in all combustion units. For pellets made of maize whole crop at least some slag was found in almost all combustion tests (except for MCp02 in boiler L6). However, considerable differences regarding the slag formation intensity were found dependent on the boiler technology used.

Table 22: Qualitative assessment of slag formation during combustion of biomass fuels in different boiler technologies

Fuel		Fuel ID	Slag formation in different boilers			
			L5	L6	L7	L8
HQ wood pellets	HQ06	-	-	-	-	
Maize whole crop	MCp02	○	-	●	n/a	
	MCp03	○	●	n/a	●	
Straw	STp01	●●	●●	●●	n/a	
	STp03	n/a	●	n/a	●●	
Miscanthus	MIp01	n/a	●	●	n/a	
	MIp02	-	-	n/a	-	
●●.....severe slag formation		○.....little slag formation		n/a.....not available		
●.....considerable slag formation		-.....no slag formation				

Figure 35 shows the grate section of boiler L5 when operated with straw, maize whole crop and *Miscanthus*, and differences with regard to slag formation can already be seen on the pictures: Large slag lumps formed during the combustion of straw cannot be removed (a), and slag from straw ash blocks the whole grate (b). Slag is also formed during combustion of maize whole crop (c) and (d), but lumps are smaller and most of them can be removed by the

successive fuel. Picture (e) shows the grate after the combustion of Miscanthus, and only ash without slag particles is found.



(a) STp01



(b) STp01



(c) MCp03



(d) MCp03



(e) MIp02

Figure 35: Combustion zone in boiler L5 during/after the combustion of straw (a) and (b), maize whole crop (c) and (d) and after the combustion of Miscanthus (e).

Quantitative assessment of slag formation has been conducted for a number of different fuel ashes from the combustion tests in boiler L8. In Figure 36 the performance of different fuels is compared based on the fraction of slag particles in the ash, and results are shown for two different boiler settings. (For particular fuels more frequent grate cleaning intervals were necessary in order to enable a stable boiler operation.) Although a certain influence of grate cleaning intervals on slag formation is obvious, a basic conjoint assessment of the investigated fuels is reasonable.

No slag formation was found after reference tests with HQ wood, and no or only very little slag was formed during combustion of Miscanthus. Some smaller slag particles were found after the combustion of pellets made of vineyard pruning, but they did not affect the combustion process. Large slag particles were found in the combustion residues from wheat bran, giant reed and straw, amounting to fractions of around 40 % of total ash. Similar slag fractions were found for sorghum bicolor and maize whole crop, but with a larger number of small particles (4 – 5.6 mm).

The investigated hay samples showed considerable differences regarding their slag formation tendency: Only little slag was formed from *HAp06*, whereas 20 wt% and 33 wt% of the ash formed slag when burning *HAp05* and *HAp07* respectively, also showing considerable fractions of large particles.

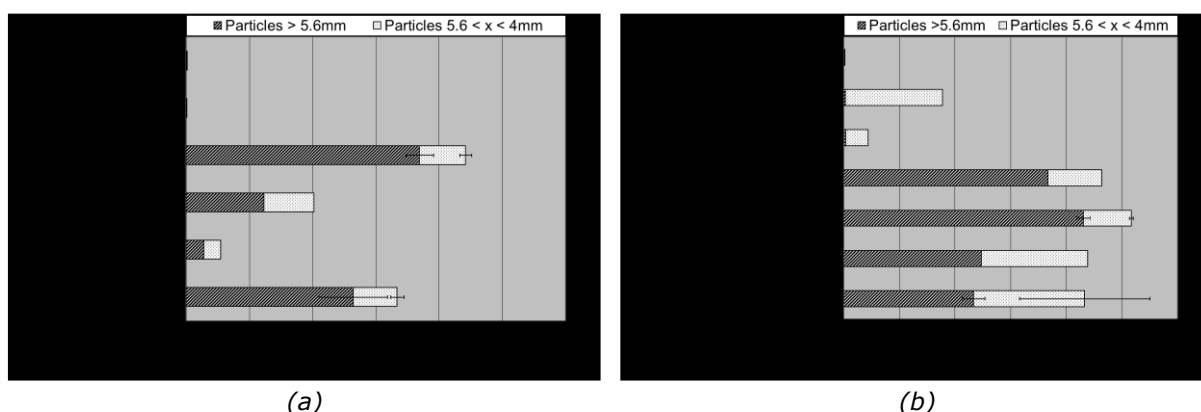


Figure 36: Quantitative evaluation of slag formation from the combustion of different fuels in boiler L8 for standard grate cleaning settings (a) and more frequent grate cleaning intervals (b).

Comparison of fuel properties

For the fuels where quantitative assessment of the slag formation is available, ash content and characteristic melting temperatures (SOT and FT) as well as elemental composition in terms of main ash forming elements are shown in Table 23 and Figure 37 respectively.

Table 23: Ash content, softening temperature (SOT) and flow temperature (FT) of the fuels shown in Figure 36 (a) and (b) respectively.

Fuel in Figure 36 (a)	a	SOT	FT	Fuel in Figure 36 (b)	a	SOT	FT
HQ wood (HQ06)	0.3	1370	1470	HQ wood (HQ06)	0.3	1370	1470
Miscanthus (MIp09)	2.9	1172	1260	Vine pruning (OTp07)	2.6	795	> 1450
Wheat bran (OTp03)	5.7	670	940	Miscanthus (MIp02)	3.3	1010	> 1400
Hay (HAp05)	9.6	820	1180	Giant reed (OTp05)	4.9	893	1169
Hay (HAp06)	6.0	870	1180	Straw (STp03)	5.7	800	1080
Hay (HAp07)	7.1	840	1210	Sorg. Bic. (OTp09)	6.3	990	1080
				Maize w. crop (MCp03)	3.4	910	990

No correlation can be found between ash content and slag formation tendency: Slag fractions differ considerably for fuels with similar ash contents like e.g. wheat bran *OTp03* and hay *HAp06* in Figure 36 (a) and Miscanthus *MIp03* and maize whole crop *MCp03* in Figure 36 (b).

For the investigated fuels, a simple qualitative relation is found between severity of slag formation and characteristic ash melting temperatures: For fuels with a softening temperature (SOT) above 1000 °C no or only very little slag formation is observed, whereas fuels showing lower SOT-values show an increased slag formation tendency. Apart from that differentiation no more significant information is obtained from the characteristic temperatures: E.g. SOT-values of the three hay-samples are very similar unlike their considerably different slag formation performance in real combustion tests. Moreover, trouble-free operation is possible using vine pruning pellets, despite their relatively low SOT of 795 °C. The highest flow temperature is found for *HAp07*, although this is the hay sample with the most distinct slag formation tendency.

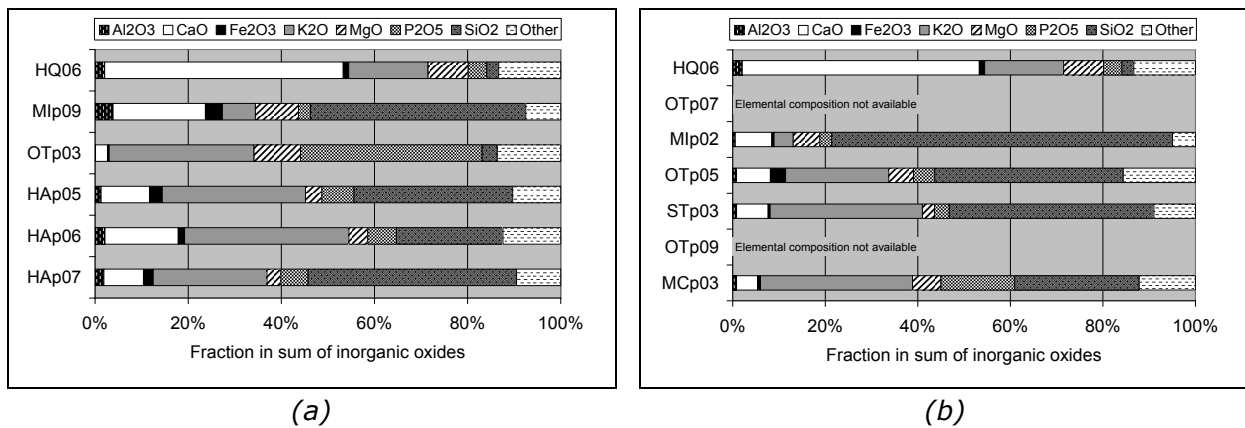


Figure 37: Elemental composition of the investigated fuels shown in Figure 36.

It has been found previously, that no slag formation tendency is observed for wood ashes with a high Ca-fraction and a low Si-content [e.g. ÖHMAN 2004 (1)]. Increased concentrations of Si and also P together with increased amounts of alkaline metals as typically found in non-woody biomass fuels enable the formation of low-melting silica-compounds and consequently cause slag formation. (cf. e.g. LINDSTRÖM 2007, GILBE 2008 (1) or LINDSTRÖM 2008)

The investigated fuels basically follow this trend: No slag formation is observed for HQ-wood pellets. The slag formation tendency of hay samples increases with decreasing Ca- and increasing Si-concentrations. No or only little slag is formed from both Miscanthus samples, also containing large amounts of Si but relatively low K-concentrations. All other non-woody biomass – except Miscanthus – formed considerable amounts of slag: The ashes of giant reed and straw contain high concentrations of both Si and K (41 % and 45 % SiO_2 and 22 % and 23 % K_2O respectively in the ash), and considerable amounts of P and K were found in the ash of wheat bran and maize whole crop.

Considering the results from exploratory data analysis in chapter 5.1, it is found that all slagging fuels – except Miscanthus sample *MI01* – are assigned to either group 4 or group 5 determined via k-means clustering. More specific conclusions regarding the slagging behavior are not possible based on the results from exploratory data analysis.

5.4.2 Variation and improvement of wood pellets

Compared to other biomass raw materials, wood pellets are considered as a convenient and unproblematic fuel regarding slagging problems, emissions, deposit formation and corrosion. However, numerous incidents due to slag formation on the grate/in the combustion zone after combustion of wood pellets have been reported – even for ÖNORM M 7135-conform fuels. Problems have been related to various possible causes like e.g. wood species (e.g. hard wood), non-mineral additives, the raw material fraction, non-certified pellet production, imported products or an increased share of fines.

In the present chapter the influence of the raw material basis on the pellets quality and the slagging behaviour in particular is evaluated following two different approaches: Lab-scale combustion tests are conducted using specially produced wood pellets with systematically varied raw materials. On the other hand the ash melting properties of various problematic wood pellet qualities from all over Europe are studied. Investigations are aiming at showing the range of variation of commercially available wood pellets for small-scale combustion and an evaluation of raw-material related influencing factors on slag formation.

5.4.2.1 Wood pellets test series I – Impact of the raw material basis

Various wood pellets were produced under well-controlled conditions covering different raw materials and non-mineral additives. Thereby, it was intended that fuels should come up, or only slightly exceed the required fuel properties according to ÖNORM M 7135. Choosing the raw materials the following aspects have been considered:

- Wood species: spruce, pine, larch
- Raw material fraction: bark, grinding dust, sawdust, wood shavings
- Non-mineral additives: shredded maize, rye flour, starch

Pellets made of pure spruce sawdust were chosen as a reference material, since spruce is the main raw material for pellets production in Austria.

Pellets made of 100 % pine and larch were tested to study the combustion behaviour of different wood species. In order to investigate the effect of different raw material fractions,

pellets made of dust from wood grinding and wood shavings as well as pellets with a certain percentage of bark have been used. Abrasion of tools and enrichment or depletion of certain elements in particular fractions from wood processing industry were assumed as potential reasons for differences in the properties of wood shavings or dust. Small amounts (about 1 %) of organic products like e.g. starch are frequently used as additives in order to improve the pelletising process as well as the mechanic properties of the pellets. The potential impact of such additives was studied as well.

In order to evaluate the ash melting properties of the investigated fuels, combustion tests were conducted in 5 different state-of-the-art small-scale pellet boilers. Showing high demands on the fuel quality boiler L1 was chosen as reference unit where all fuels were studied. Pellets were burnt under well-controlled conditions, and the slagging behaviour was assessed qualitatively after several hours (varying dependent on the combustion unit) of full-load operation. Table 24 gives an overview about the slag formation of the investigated fuels in the different boilers. Pictures of the remaining slag particles are presented in Figure 38.

Table 24: Qualitative assessment of slag formation during combustion of various wood pellets in different combustion technologies. (adapted from FRIEDL 2006)

Fuel ID	Fuel Description	Number of units with observed slag formation tendency			Boiler				
		●	○	-	L1 R _{HQ}	L3	L4	L5	L6
HQ01	Spruce (sawdust)	0	0	5	-	n.t.	n.t.	n.t.	n.t.
HQ04	Spruce (sawdust)	0	0	5	-	n.t.	n.t.	n.t.	n.t.
HQ05	Spruce (sawdust)	0	0	5	-	-	-	-	-
LQ01	Spruce with ~2 % bark	0	1	4	○	-	-	-	-
LQ02	Spruce with ~5 % bark	1	2	2	○	-	-	-	○
HQ09	Spruce with ~5 % starch	0	0	2	-	n.t.	n.t.	n.t.	-
HQ12	Spruce with ~5 % shredded maize	0	1	4	-	-	-	-*)	-
HQ15	Spruce with ~5 % rye flour	0	1	3	-	-	-	n.t.	-
HQ16	Spruce (wood shavings)	0	0	2	-	n.t.	n.t.	-	n.t.
HQ17	Spruce (grinding dust)	0	0	2	-	n.t.	n.t.	-	n.t.
HQ18	Pine (sawdust)	0	1	4	-	○#)	-	-*)	-
HQ19	Larch (sawdust)	1	1	3	●	-	○	-*)	-
●●.....Severe slag formation		○.....Little slag formation			n.t.....Not tested				
●.....Considerable slag formation		-.....No slag formation							

^{+) R_{HQ}.....Reference boiler for HQ wood pellets}

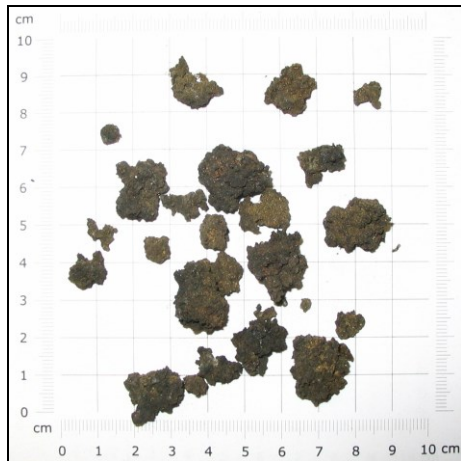
^{*)} In one combustion unit little slag-type deposits were found on a thermocouple coverage. As long as no other slag formation was observed, the results were considered with "no slag". Possibly an increased slag formation probability of the fuel can be assumed.

^{#)} power outage

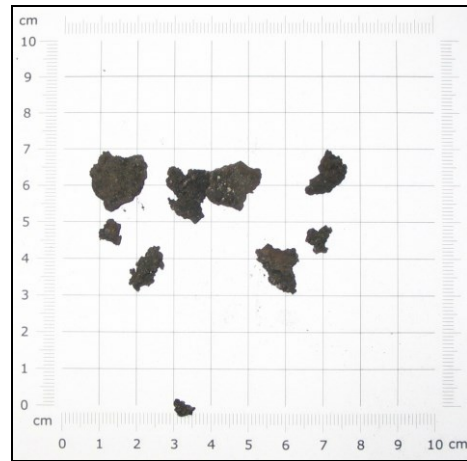
Combustion performance – slagging behaviour

Wood species: Almost no slag was formed in any of the pellet boilers during combustion of pellets of 100 % pine. Only in boiler L3, slag particles were found after a break down due to power outage. Therefore, no slag formation from the combustion of pine is determined, and an increased slag formation propensity of the fuel can only be assumed due to the slag particles after the breakdown and the slag-like deposits on the thermocouple coverage in boiler L5.

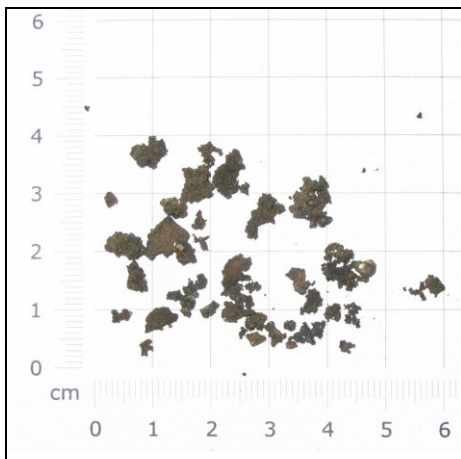
After the combustion of larch pellets slag was found in 2 out of 5 combustion units. In one unit several slag particles of about 2 cm were found in the burner pot after 72 h under full load operation. At this time, no severe effects on the combustion process but slightly increased CO emissions at the end of the combustion test were observed. Since the slag particles could not be removed automatically, a breakdown of the combustion process with increasing operating time is possible.



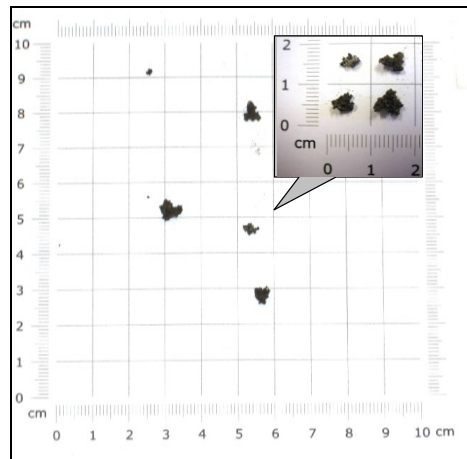
(a) HQ19 larch (sawdust)
boiler L1



(b) HQ19 larch (sawdust)
boiler L4



(c) LQ02 spruce with ~5 % bark
boiler L1



(d) LQ02 spruce with ~5 % bark
boiler L6

Figure 38: Slag particles after the combustion of larch in boiler L1 (a) and L4 (b) and spruce with ~5% bark in boiler L1 (c) and L6 (d). [FRIEDL 2006]

Raw material fraction: By-products of wood without bark (i.e. sawdust, wood shavings and dust) did not show considerable differences with regard to slag formation. However, significant influence could be observed for pellets containing certain amounts of bark. Moreover, an increase of both slag formation tendency and amount of slag was found with increasing fractions of bark in the raw material.

Addition of organic binders: No significant influence of organic additives on the slag formation tendency was found: As expected, no slag formation could be observed during the combustion of wood pellets with 5 % starch, since starch only consists of C and H. After the combustion of pellets with 5 % shredded maize and 5 % rye flour no slag was formed in all combustion units investigated, and an increased slag formation propensity of the fuel can only be assumed for the pellets with shredded maize due to slag-like deposits on the thermocouple coverage in boiler L5.

Comparison of fuel properties

Fuels were analysed in order to investigate potential indicators for increased slag formation tendency. The main differences with regard to elemental composition, ash content and characteristic melting temperatures are summarised in Table 25.

Table 25: Summary of fuel properties of the investigated pellets and comparison with reference fuels (pellets that formed slag are marked with bold letters)

Fuel ID	Fuel description	Characteristic temperatures		Ash content	Increased elemental concentration for
		SOT in °C	FT in °C		
HQ01	Spruce	1360	1470	0.29	Reference
HQ04	Spruce	1370	1430	0.36	Reference
HQ05	Spruce	1350	1430	0.36	Reference
LQ01	Spruce with ~2 % bark	1359	1460	0.34	Al, Fe, Si
LQ02	Spruce with ~5 % bark	1347	1460	0.59	Al, Fe, Si (Ca, Mg, P)
HQ09	Spruce with ~5 % starch	1380	1430	0.29	not observed
HQ12	Spruce with ~5 % shredded maize	1500	1430	0.33	P, S (K)
HQ15	Spruce with ~5 % rye flour	1480	1470	0.21	P, S (K)
HQ16	Spruce (wood shavings)	1380	1400	0.21	not observed
HQ17	Spruce (grinding dust)	1380	1390	0.22	S, N
HQ18	Pine (sawdust)	1340	1450	0.25	not observed
HQ19	Larch (sawdust)	1390	1430	0.31	Si

In general the quality of the tested pellets was very good, and regarding the fuel properties almost all of them complied with the requirements according to ÖNORM M 7135 - except the pellets with 5 % bark due to the increased ash content.

For all investigated fuels no considerable difference could be found regarding the characteristic melting temperatures. Values are found to be equal or even above the reference temperature of high quality spruce pellets with 1360° for SOT and 1470 °C for FT. The ash content was as twice as high for pellets with 5 % bark when compared to the reference fuel, and slightly increased for pellets containing 2 % bark – but significantly below the threshold value according to ÖNORM M 7135. The ash content of *LQ02* at least indicates the different raw material basis, but neither the characteristic temperatures nor the ash content indicate the increased slag formation tendency of *LQ01* and *HQ19*.

Regarding the elemental composition, a significant increase of Si could be observed for all slag forming pellets: The Si-content was doubled for pellets made of larch, and increased by factor 3 and 7 for pellets containing 2 % and 5 % of bark respectively. Moreover, a significant increase of Al and Fe was found for bark-containing pellets and minor changes with regard to Ca, Mg and P could be observed. For pellets containing shredded maize and rye flour mainly changes with regard to P and S as well as slightly increased values for K could be observed. This change of particular elements consequently causes a change of the proportions in the ash mixture. The fractions of elemental oxides for the investigated fuels are shown in Figure 39.

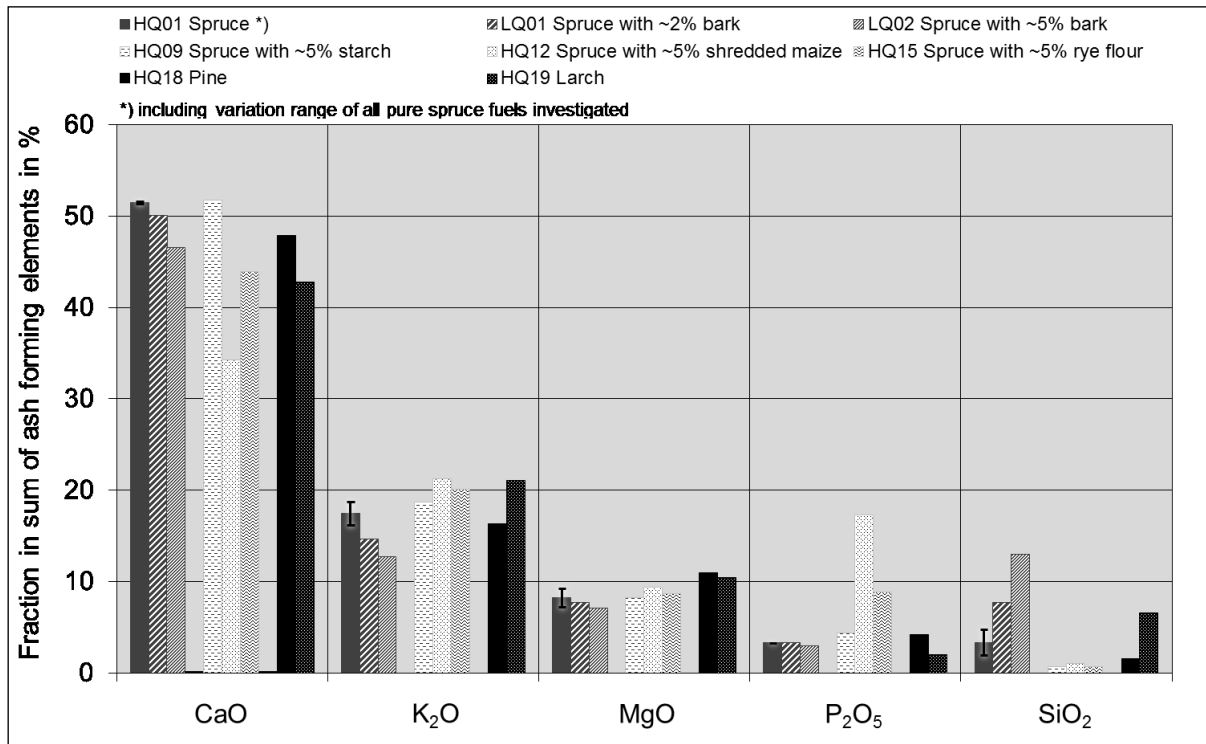


Figure 39: Fractions of the main oxides in sum of ash forming elements for selected wood pellets. For HQ01 the variation range of all pure spruce samples investigated is marked.

The strong rise of Si due to the addition of bark led to reduced proportions of Ca, Mg and K in the ash mixture, even though the content of Ca and Mg increased compared to pure spruce. The addition of starch did not show significant effects on the elemental composition, but the utilisation of grain-products caused a clear increase of P in the mixture together with a reduction of Ca. This effect was found to be much stronger for maize than for rye. No significant difference could be found comparing the elemental composition of pine and spruce. However, increased amounts of Si and K and a lower Ca-content were found for pellets made of larch. These results are in good accordance with previous findings where Si and K are considered as slag-increasing elements, whereas a slag reducing or even preventing effect is attributed to Ca. An increased proportion of P₂O₅ together with a reduction of CaO as caused by the addition of grain-products may also lead to a higher slag formation tendency. However, an addition of 5 % does not seem to be problematic in this regard.

Comparing the experimental performance to the findings from exploratory data analysis in chapter 5.1 good accordance is found: The slag forming samples *LQ01* and *LQ02* are clearly distant to HQ wood samples, being part of the widespread group of LQ wood scores, and also *HQ19* is located in the fringe area of the HQ wood cluster, showing a significant distance to the dense centre of HQ wood scores. According to the cluster analysis all three samples are either assigned to the HQ wood cluster or at least are located very close to that cluster, in spite of their increased slag formation tendency. This can be explained with the fact that all three pellets (i.e. *LQ01*, *LQ02* and *HQ19*) were produced under well controlled conditions, and thus changes with regard to elemental composition are only caused by different raw materials and not e.g. by soil contamination.

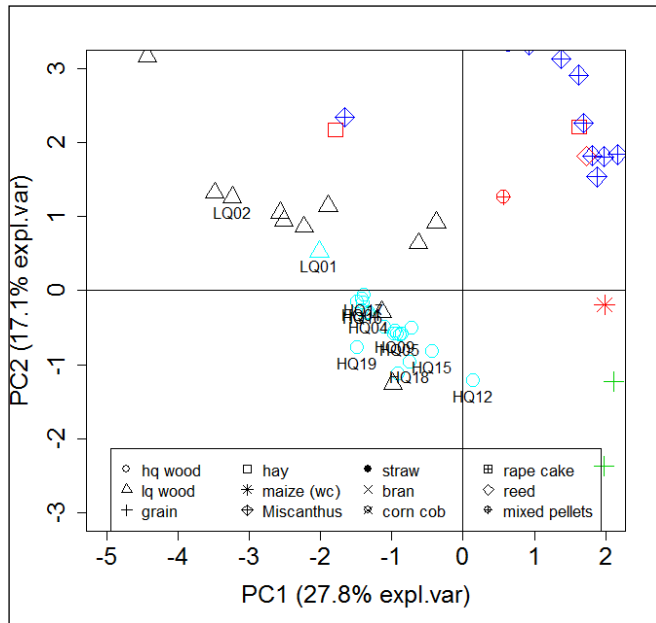


Figure 40: Detail of the PCA-plot (PC1 vs. PC2) discussed in chapter 5.1 showing the wood pellets cluster. (Only investigated pellets are labelled.)

Though no slag formation was observed for these fuels, samples *HQ18*, *HQ15* and particularly *HQ12* are found at the fringes of the HQ wood cluster, and thus represent the admixture of the different additives.

5.4.2.2 Wood pellets test series II – Investigation of problematic wood pellet qualities

From a set of commercially available wood pellets dedicated for the combustion in small-scale applications, a number of samples has been chosen preferring fuels that were reported to cause slag related problems or showing high ash contents. Moreover, 2 types of pellets were investigated consisting of wood as main fraction and a certain amount of non-woody biomass i.e. straw and corn cob residues.

A standard procedure was defined in order to evaluate the slag formation tendency of different wood pellets: Each fuel was tested at 4 different settings varying the grate cleaning intervals, and the slag formation was evaluated qualitatively by determining the amount of residual ash and slag in the burner pot after the experiment. Table 26 gives an overview about the slag formation tendency of the investigated wood pellets for 4 different grate cleaning intervals. The slag formation intensity is presented as the fraction of slag in the burner pot in relation to the total mass of combustion residues.

Table 26: Slag formation during combustion of different wood pellet qualities for 4 different settings varying the grate cleaning interval (adapted from WOPIENKA 2008)

Fuel (origin)	Cleaning interval ^{*)}			
	I 80 min.	II 140 min.	III 200 min.	IV 360 min.
Reference-pellets (ÖNORM standard)	-	n.t.	n.t.	-
LQ09 (Germany)	-	n.t.	n.t.	-
LQ10 (Germany)	-	n.t.	n.t.	-
LQ11 (Germany)	-	n.t.	n.t.	-
LQ13 (France)	-	n.t.	-	o
LQ14 (Norway)	-	n.t.	n.t.	-
LQ15 (Romania)	••	•••	•••	•••
LQ17 (Slovakia)	••	•	•	••
LQ18 (Spain)	-	n.t.	-	o
LQ19 (UK)	o	•	••	•
Mx01 (tailor-made)	o	•	•	••
Mx02 (tailor-made)	•••	•••	•••	•••
Explanation: Fraction of slag in the burner pot in relation to the total mass of combustion residues.	- No slag o < 10 % • 10-30 % •• 30-50 % ••• >50 % n.t.....Not tested			

^{*)} Intervals I and IV are standard intervals, interval II and III are only tested is slag formation is observed in interval III and IV respectively.

Combustion performance – slagging behaviour

Considerable slag formation was shown for 5 pellet samples. For these pellets slag on the grate was even observed when using the shortest cleaning interval. This was particularly observed for *LQ15*, *LQ17* and the mixed pellets with 10 % straw *Mx02*. Although showing slag formation for all grate cleaning settings, minor slag formation was found for *LQ19* and the mixed pellets with corn cob residues *Mx01*.

LQ13 and *LQ18* also showed an increased slag formation tendency, but slag particles in the burner pot were only found for the setting with the least number of grate cleanings. The pictures in Figure 41 show slag formation of sample *LQ15* and *LQ19* both operated with grate cleaning interval IV.

Qualitative description of slag lumps and particles

Variations were observed with regard to durability and visual nature of the slags formed. Therefore, a brief description and comparison of the slag samples shown in Figure 42 is given below.

After combustion of ***LQ13*** slag in the burner pot was only found when using the most demanding setting (interval IV). The dark grey porous agglomerates were unstable and easy to break.

On closer inspection of **LQ15** orange deposits and small white dots were found on the light grey slag particles, probably related to Fe-containing compounds and K- and Cl-salts respectively. Even though glass-like molten areas were found on the particle surfaces, the slag was not very stable and easy to break due to the high porosity. Average size of the agglomerates did not exceed 2 cm.

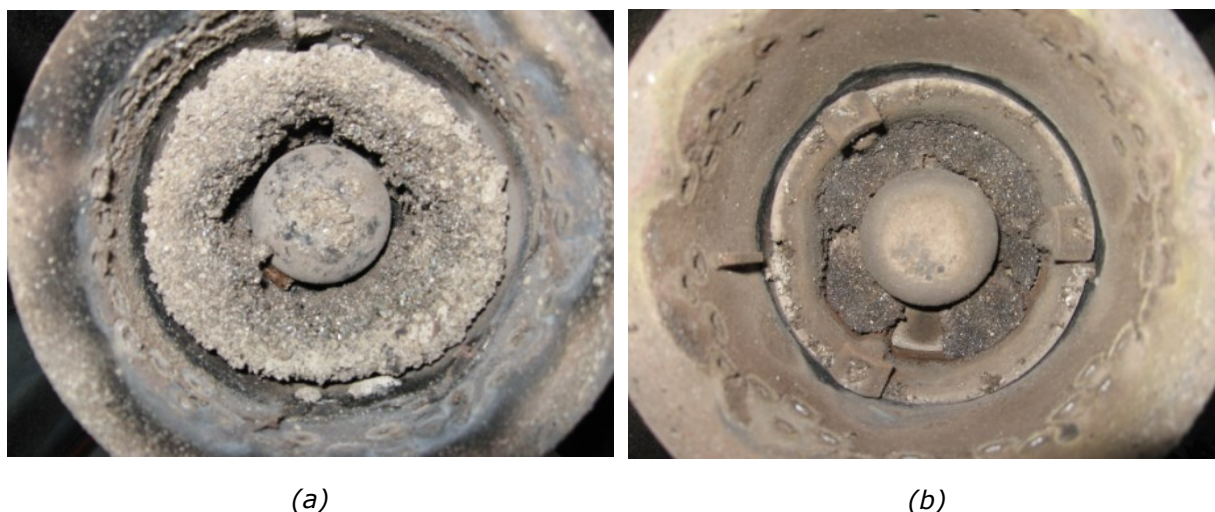


Figure 41: Slag formation in the burner pot for (a) LQ15 and (b) LQ19 (interval IV) [WOPIENKA 2008]

Very dense and stable dark grey slag was formed from ash of **LQ17** also showing white dots like slag from LQ15. The average size of slag lumps was below 1 cm, and particles did not stick to each other.

Slag from **LQ18** was small-grained, easily to break, and the size of agglomerates did not exceed 0.3 cm. Moreover, these pellets showed the lowest slag fraction formed.

Small and dark grey slag lumps with an average size below 0.5 cm were left after combustion of **LQ19**. Despite showing fragile slag structures at the surface, these agglomerates were of considerable mechanical stability. For these pellets, also some scattered white dots were found.

Slag formed by the mixed pellets with corn cob residues **Mx01** showed a completely different characteristic than slags from pure woody raw materials. Instead of individual slag lumps a continuous ring was formed that broke to pieces when removed from the burner pot. Dark green and violet structures were observed on the slag surface, eventually caused by Fe- or K-compounds, and highly molten formations were found on the bottom-side.

The most intensive slag formation was obtained from the combustion of mixed pellets with straw addition **Mx02**. Compact agglomerates of an average size of 3 cm stuck to each other and also showed violet and some green structures.

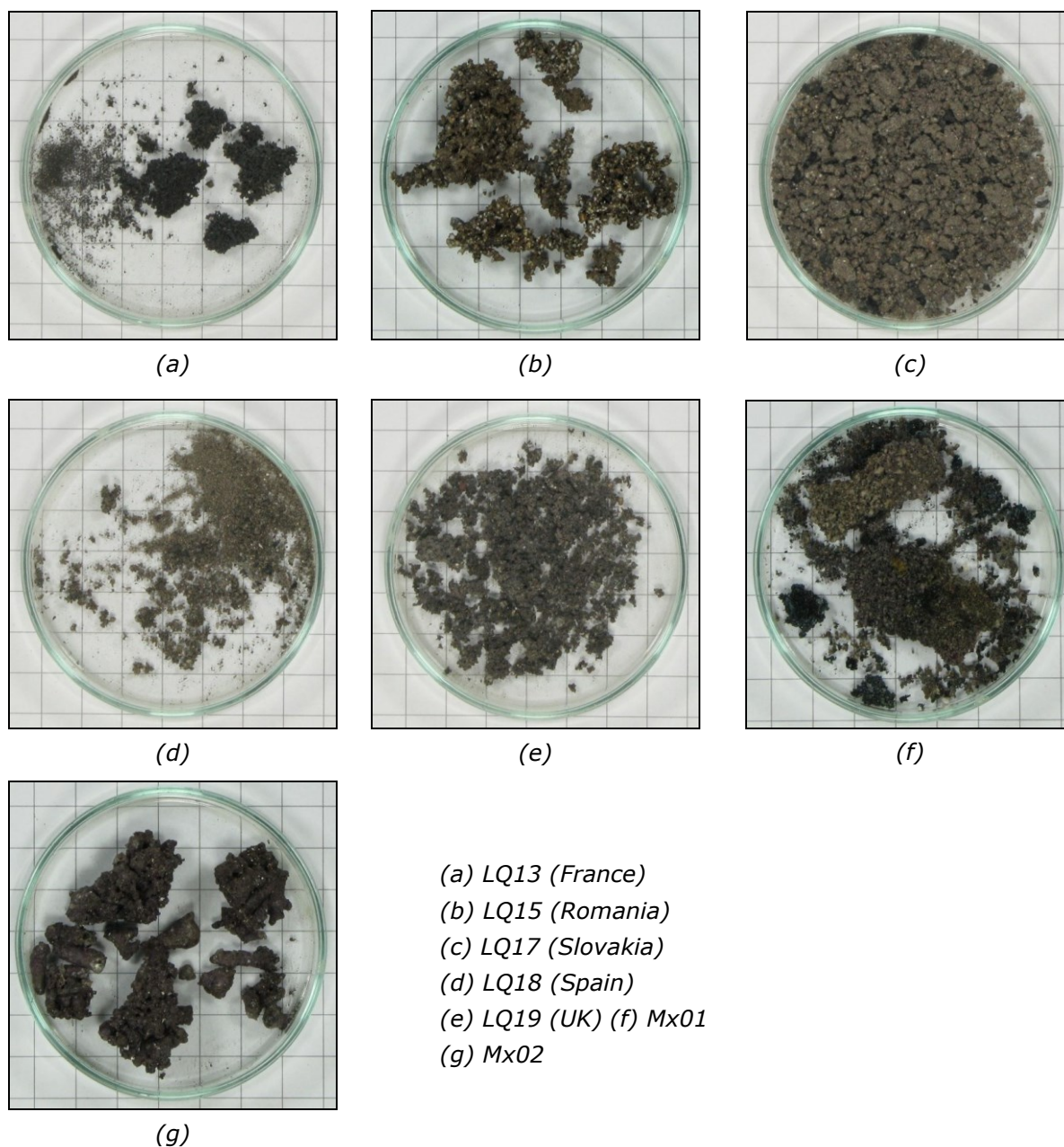


Figure 42: Slag samples from the combustion tests with interval IV [WOPIENKA 2008]

Comparison of fuel properties

Differences with regard to slag formation tendency were analysed considering the fuel properties in terms of ash content, characteristic melting temperatures and elemental composition. An overview about the main analyses results is given in Table 27.

Regarding the ash content, all pellets that were operated without any slag formation meet the requirements for Class A1 pellets according to ÖNORM EN 14961-2. On the other hand slag formation was observed for two samples that comply with this standard anyhow.

Table 27: Summary of fuel properties of the investigated pellets (pellets that formed slag are marked with bold letters)

Fuel	Characteristic melting temperature		Ash content	Increased elemental concentration
	SOT in °C	FT in °C		
Reference-pellets (ÖNORM standard)	1370	1470	0.25	Reference
LQ09 (Germany)	1230	1360	0.26	not observed
LQ10 (Germany)	1230	1270	0.33	not observed
LQ11 (Germany)	1420	> 1460	0.34	not observed
LQ13 (France)	1020	1430	0.36	Fe
LQ14 (Norway)	1320	1450	0.32	not observed
LQ15 (Romania)	1180	1230	2.06	Si, Fe, Al
LQ17 (Slovakia)	1120	1250	1.28	Si, Fe, Al
LQ18 (Spain)	1390	1430	0.67	Al
LQ19 (UK)	1290	1330	0.93	Fe
Mx01 (tailor-made)	1400	> 1460	1.13	Si, K
Mx02 (tailor-made)	1020	1430	0.83	Si, K

An increased slag formation tendency with increasing ash content and decreasing Flow Temperature was found for the investigated wood pellets, and trends are shown in Figure 43. However, no such tendency could be detected for the Softening Temperature: Only minor slag formation was observed for sample *LQ13* despite the relatively low Softening Temperatures of 1020 °C, and contrariwise large amounts of slag were found from the combustion of *LQ15* compared to other fuels with similar SOT-values. However, *LQ15* is the fuel showing also the highest ash content among the investigated samples.

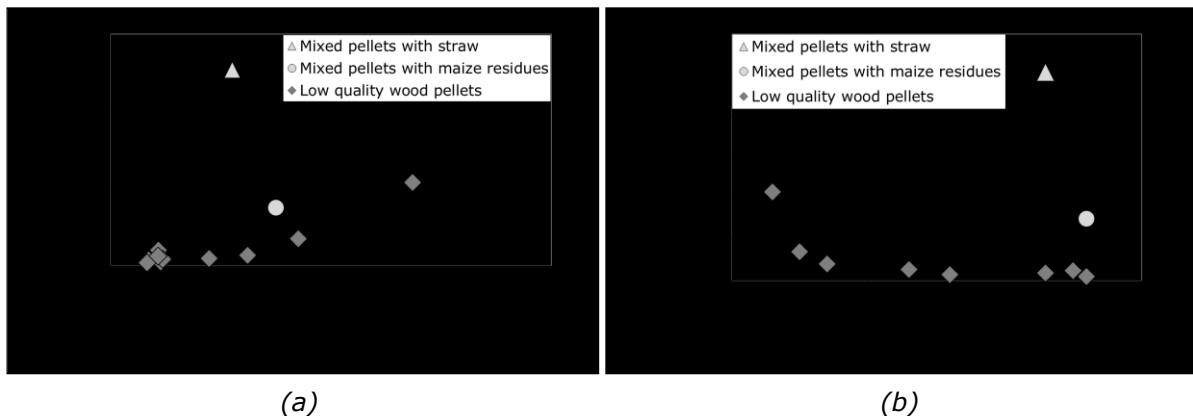


Figure 43: Fraction of slag in total combustion residues (interval IV) versus ash content (a) and Flow Temperature (b). [WOPIENKA 2008]

Pellets with admixtures of non-woody raw materials (i.e. straw and corn cob residues) totally differed from these trends: Considerable amounts of slag were formed, despite both samples show a comparably moderate ash content and high Flow Temperatures. At least a low Softening Temperature was found for sample *Mx02* that showed the most serious slag formation performance.

Regarding the elemental composition, some basic trends are identified: All investigated pellets show an increased amount of SiO_2 in mineral matter compared to the reference pellets made of pure spruce saw dust, and particularly large fractions are found for all pellets that showed severe slag formation i.e. *LQ15*, *LQ17*. Among the slag forming wood pellets, the concentration of Al_2O_3 is increased for the most slagging fuels *LQ15* and *LQ17*, and also for *LQ18*. Increased concentrations of Fe_2O_3 are observed for *LQ13* and *LQ19*. These findings are in good accordance with information received from some pellet producers, stating to process bark and wood chips in addition to pure stem wood. Also large amounts of SiO_2 were found for the mixed biomass pellets *Mx02*, and high concentrations of K_2O are found for both mixed biomass pellets *Mx01* and *Mx02*.

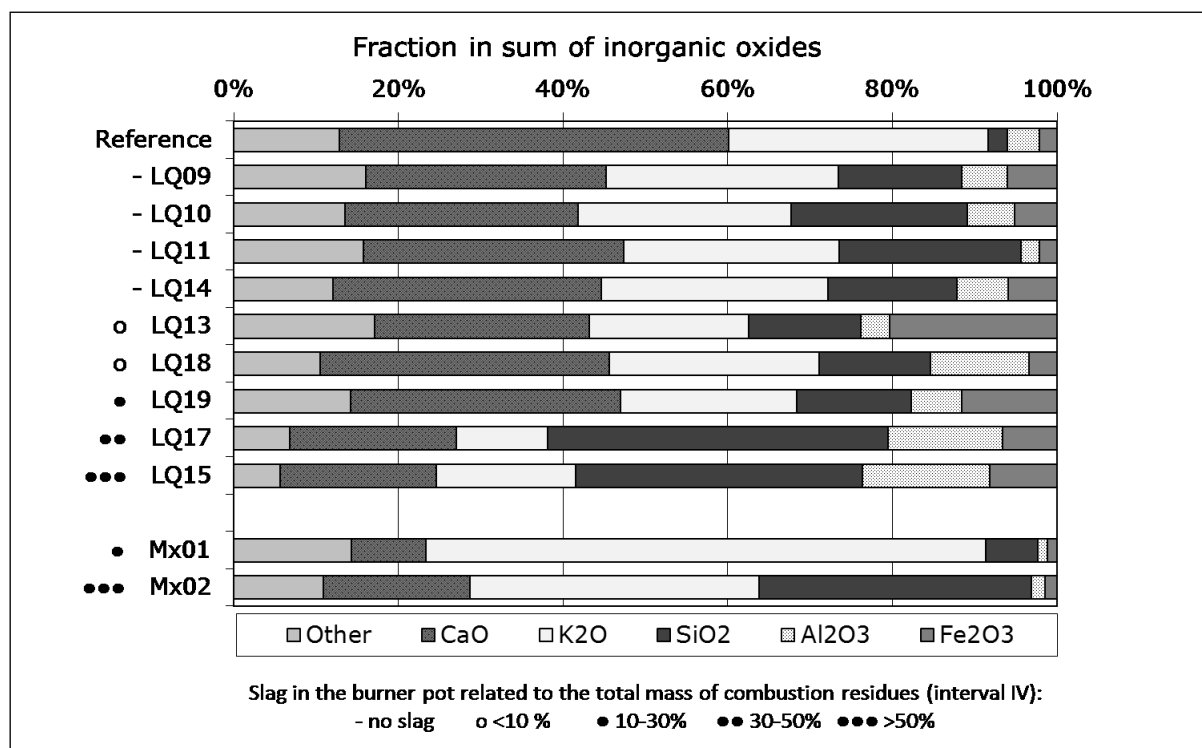


Figure 44: Fractions of the main oxides in sum of ash forming elements for the investigated wood pellets and the mixed biomass pellets. Wood pellets are ranked by increasing slag formation tendency.

These tendencies are basically in good correlation with previous results and findings from literature (cf. ÖHMAN 2004 (1), LINDSTRÖM 2008). However, neither quantitative nor qualitative conclusions about the extent of slag formation can be made based on the composition of the main ash forming constituents.

More significant information is available from the multivariate data analysis based on elemental composition: Good accordance is found when comparing the results from combustion tests (cf. Table 26) to the results of exploratory analysis in chapter 5.1: The samples *LQ15*, *LQ17*, *LQ13* and *LQ19* show the largest distance to other wood samples, and *LQ15* and *LQ17* are even assigned to a group of non woody biomass fuels (group 3 consisting of *Miscanthus* and straw samples) according to both cluster analysis methods. Also *LQ18* is located clearly distant to the non-slagging samples investigated. Samples *LQ09*, *LQ10*, *LQ11*

and *LQ14* are found closer to other HQ wood objects, and also to each other. Pellets with admixtures of straw and corn cob residues respectively (*Mx01* and *Mx02*) are located far away from woody biomass fuels as well, and are assigned to the fuel-group consisting of straw, maize whole crop and hay. Figure 45 shows the detail of the score-plot of the first two principal components with the investigated samples labeled.

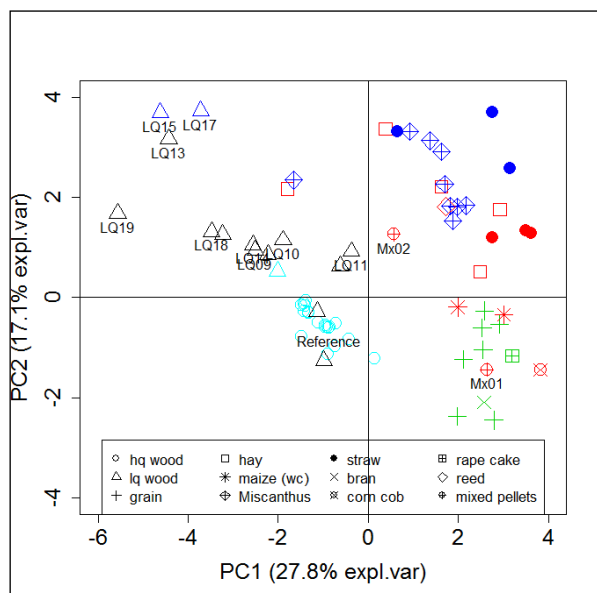


Figure 45: Detail of the score-plot (PC1 vs. PC2) discussed in chapter 5.1 showing the wood pellets cluster. (Only investigated samples are labelled.)

5.4.3 Effect of additives

The possibility of changing the elemental composition of fuels by using additives and thus improving their ash melting properties has already been discussed in section 3.3.5, and findings from previous work were presented. In the following section the effect of different types of additives is investigated in laboratory tests. In this regard both added elements and type of chemical compound are varied. Moreover, the ash melting behaviour is evaluated in practical combustion tests for selected fuels and additives.

In general, lower melting temperatures and consequently an increased slag formation propensity is found for non-woody biomass fuels. Thus, the effect of additives was investigated for different types of non-woody biomass: A broad variety of pellets was produced from straw, and selected additives were also used for Miscanthus and maize whole crop fuels. Based on previous findings learned from literature (cf. section 3.3.5) Ca-, Mg- and Al-containing additives have been chosen, and their influence on characteristic melting temperatures was investigated.

Table 28 gives an overview about the concentrations of particular elements in different additives. In order to be able to compare the effect of different types of additives, results are always referred to the amount of the investigated element instead of the amount of additive used.

Table 28: Concentration of particular elements in the investigated additives

Name	Main compound(s)	Other elements	g (Ca/Ca+Mg/Al) per g additive	mol (Ca/Ca+Mg/Al) per kg additive
Lime	CaO	-	0.68 Ca	17 Ca
Carbonate of lime	CaCO ₃	-	0.39 Ca	9.7 Ca
Dollit TM	CaCO ₃ and MgCO ₃	-	0.36 Ca/Mg	10.7 Ca/Mg
Epsomite	MgSO ₄	-	0.20 Mg	8.3 Mg
Magnesiummehl TM	CaCO ₃ and MgCO ₃	-	0.33 Ca/Mg	11.1 Ca/Mg
Mullite	Al ₄ Si ₂ O ₁₀	Si	0.38 Al	14.1 Al
AlSiH TM	n/a	Si	0.19 Al	7.2 Al
Sialin TM	n/a	Si, (K)	0.07 Al	2.7 Al
Bauxite	Oxide/Hydroxide of Al, Fe, Si	Fe, Si, Cl	0.37 Al	13.6 Al
Bentonite	(Al _{1.67} Mg _{0.33})[(OH) ₂ Si ₄ O ₁₀] · Na _{0.33} (H ₂ O) ₄	Fe, Si, (Mg, Ca, K)	0.02 Al	0.9 Al

5.4.3.1 Laboratory tests

Ash melting analyses have been conducted for different straw samples using additives containing Ca, Mg, Al and both Ca and Mg as listed in Table 28.

All investigated additives increased the characteristic melting temperatures determined in the ash melting test according to ÖNORM CEN/TS 15370, and different straw samples basically showed a similar trend when using the same additive. Dependent on the type and concentration of additive, softening temperatures in average were increased by about 250 °C-

450 °C, and flow temperatures by 100 °C – 300 °C. In Figure 46 SOT and FT are presented for different straw samples produced with the additives lime and DolliTM.

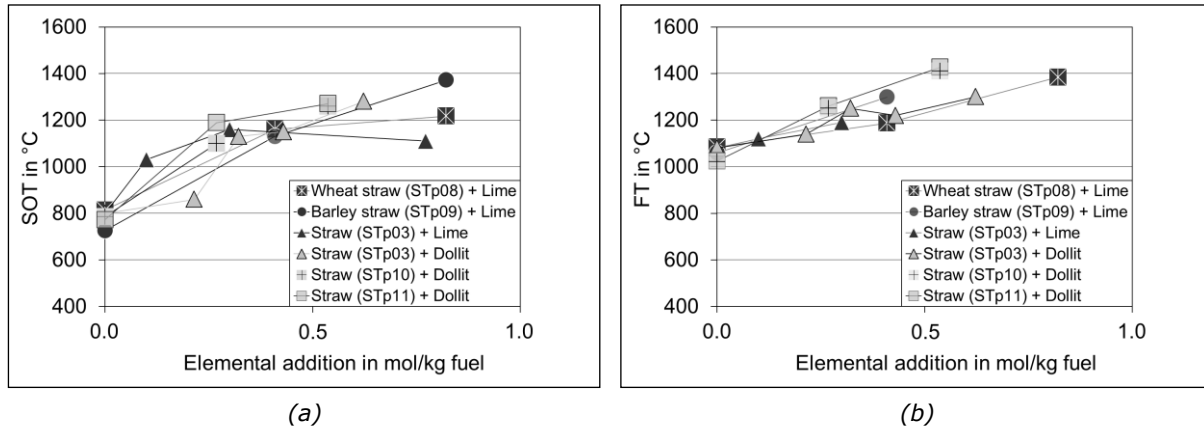


Figure 46: SOT (a) and FT (b) for different straw samples with lime and DolliTM

Both SOT and FT are clearly increasing with increasing additive addition, and variations are stronger for SOT than for FT values. Moreover, a flattening curve of the SOT characteristic for higher additive concentrations is observed for most samples, i.e. only little changes of the characteristic temperature are found with further addition.

Effect of different elements and compounds

Comparing the effectivity of different additives being applied to the same raw material, a stronger effect is observed for Al addition than for additives containing Ca or Mg. In Figure 47 characteristic temperatures are compared for samples produced from one raw material (straw STp03) with different fractions of the Al-additive mullite on one hand and the Ca-additive lime on the other hand. Both graphs show significantly higher temperatures when adding Al compared to the same amount of Ca. (Graphs refer to the molar concentration of the respective elements in the additive/fuel, and the same results are received referring to the mass fraction though).

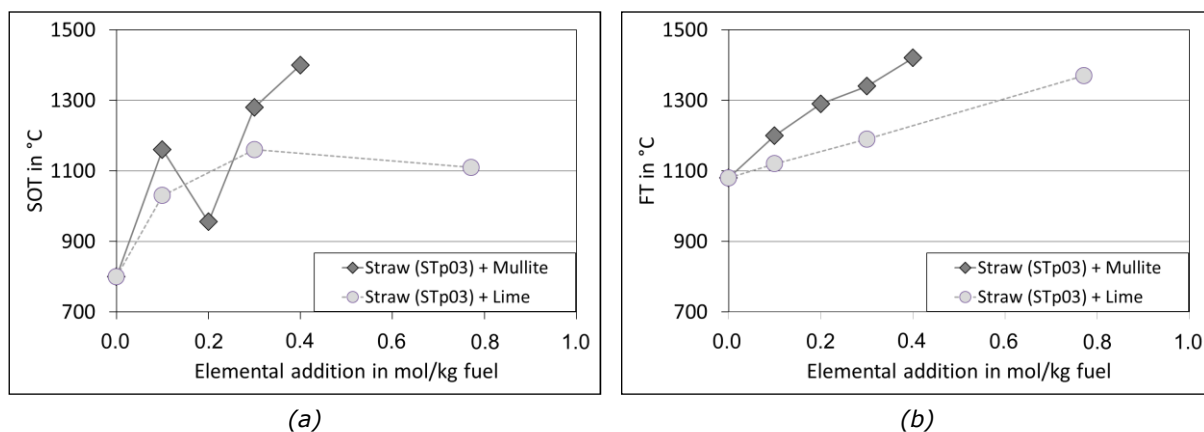


Figure 47: SOT (a) and FT (b) for fuel samples produced from one raw material with one Al-containing additive (mullite) and one Ca-containing additive (Lime).

Being both assigned to the group of alkaline earth metals, Ca and Mg are expected to show a similar effect in the fuel-additive-mixture. Figure 48 shows characteristic temperatures for straw samples produced with different additives containing Mg, Ca and both Ca and Mg. The same effect on ash melting properties is found for Mg- and Mg/Ca-additives as well as Ca- and Ca/Mg-additives, when added in the same concentration.

In addition to the elemental concentration, chemical bonds and the kind of compound respectively could also have an influence on the availability of particular elements and consequently on the effect of the additive. Regarding the investigated additives differences could neither be observed between Mg sulphate and carbonate nor for Ca carbonate or oxide.

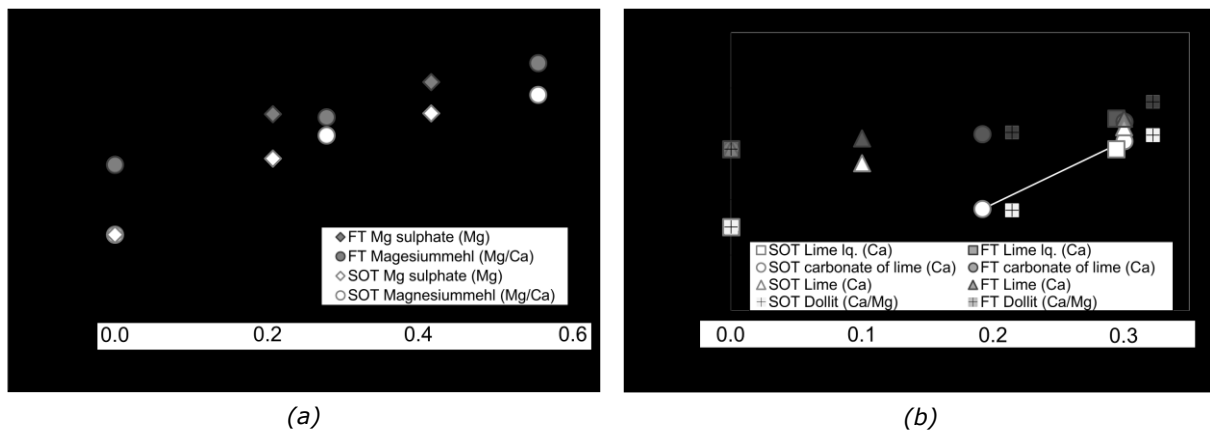


Figure 48: Characteristic temperatures (SOT and FT) for two straw samples with different Mg- and Mg/Ca-additives (a) as well as different Ca- and Ca/Mg-additives.

However, considerable variations are found when comparing the different Al-containing additives. SOT values for fuels with the same amount of Al added are widespread over a temperature range of up to 300 °C. Even though better agreement is observed for the FT values differences of 100 °C – 200 °C are determined. In Figure 49 softening temperatures and flow temperatures for fuel samples produced with different Al-containing additives are presented.

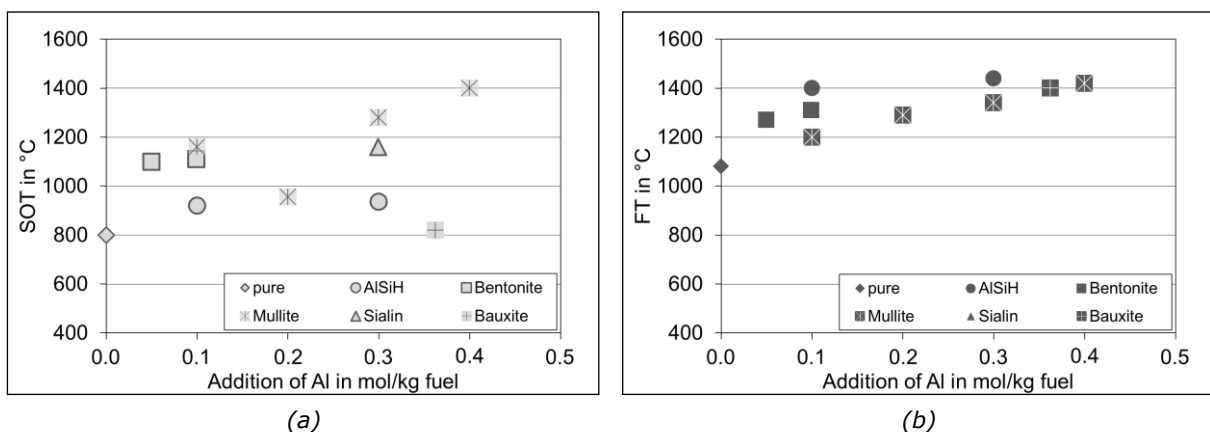


Figure 49: SOT (a) and FT (b) for fuel samples produced with different Al-containing additives.

Compounds in Ca- and Mg-containing additives only consist of elements that are released during combustion i.e. carbon and oxygen, and thus do not influence the ash composition and melting properties. Also sulphur from Epsomite is partly released, and remaining fractions do not play a major role in ash reactions. Accompanying elements in Al-containing additives – mostly Si and Fe but also K, Mg and Ca – on the other hand considerably change the ash composition and consequently the melting behaviour in different ways.

Qualitative assessment of the fuel ashes

For some samples unusual ash behaviour was observed during sample preparation and conduction of the ash melting test: An atypical characteristic was found for the change of shape with increasing temperature showing strong expansion prior to shrinking or changes in shape that were not detected by the method being not characteristic in terms of DIN 51730 (Discussion about conducted ash melting analyses with Emmanuel Padouvas, Vienna University of Technology, August 2005).

In a qualitative experiment, a small amount of pellets was burnt at 815 °C without further sample preparation, and the resulting ash was assessed qualitatively. Although high softening temperatures had been determined in the ash melting test, sticky ash samples were observed even at this temperature mainly for fuels that were produced with Si- and Al-containing additives like bentonite, mullite and Sialin™.

This discrepancy may be explained by the formation of a kind of skeleton stabilising the shape of the test specimen. Thus, first sintering or melt formation could be undetected by visual evaluation in the microscope, and changes in shape would only take place at higher temperatures. In this case, only limited conclusions regarding the slag formation propensity could be drawn based on characteristic temperatures determined via ash fusion test. (Discussion about conducted ash melting analyses with Emmanuel Padouvas, Vienna University of Technology, August 2005)

5.4.3.2 Experimental evaluation

In addition to laboratory analyses, the effect of additives on the slag formation tendency was evaluated in combustion tests in state-of-the-art small-scale combustion systems. Straw, Miscanthus and maize whole crop as well as Dollit™ and Bauxit were chosen as fuels and additives respectively. Combustion tests were conducted in different boilers under well-controlled conditions, and the slagging behaviour was assessed qualitatively after a defined period of stable operation. (In some cases, experiments had to be stopped earlier due to severe slag formation or overloaded ash box.) A quantitative assessment of the slag formed was done for different types of biomass fired in one type of boiler. In Table 29, the qualitative assessment of the combustion performance in terms of slag formation is shown for different fuel samples and combustion units.

Hardly any differences could be observed between **straw** without additive and straw with Dollit™. Both fuels showed considerable slag formation in all three boilers applied, and only in boiler L7 little improvement was observed for straw with Dollit™, slightly decreasing the size of slag particles. Also considerable slag formation was observed for straw with bauxite, but slag lumps tended to be smaller showing less molten structures, and thus were easier to

handle. The same effect was found for the second raw material (*STp03* and *STa06*) where the formation of molten areas was prevented and ash lumps were less stable for straw with bauxite compared to pure straw. However, the combustion process was strongly affected by all straw fuels.

Table 29: Qualitative assessment of slag formation during combustion of fuels with and without additives in different combustion technologies (adapted from CARVALHO 2007)

Fuel	Fuel ID	Slag formation in different boilers			
		L5	L6	L7	L8
Straw (pure)	STp01	●●	●●	●●	n.t.
Straw with Dollit TM	STa02	●●	●●	●	n.t.
Straw with bauxite	STa03	●	●	●	n.t.
Straw (pure)	STp03	n.t.	●	n.t.	●●
Straw with bauxite	STa06	n.t.	●	n.t.	●
Miscanthus (pure)	MIp02	-	-	n.t.	-
Miscanthus with Dollit TM	MIa01	-	○	n.t.	○
Miscanthus with bauxite	MIa02		○	n.t.	○
Maize whole crop (pure)	MCp03	○	●	n.t.	●
Maize whole crop with Dollit TM	MCa05	○	○	n.t.	-
●●.....Severe slag formation		○.....Little slag formation		n.t.....Not tested	
●.....Considerable slag formation		-.....No slag formation			

After the combustion of **Miscanthus** without additive, no slag was formed in all three boilers. In boiler L6 some sintered structures were found, but they were easily breakable on contact. After the combustion of Miscanthus with DollitTM some slag was found in boiler L6 and L8, and in boiler L6 even molten fractions were found. However no slag formation was observed in boiler L5. For Miscanthus with bauxite no slag was found in boiler L6, except some easily breakable sinter lumps, and sintered ash lumps including very small slag particles were also found in boiler L8.

Some slag was found in all three boilers applied after the combustion of pure **maize whole crop** pellets. Using pellets with DollitTM no slag was formed in boiler L8, and only a small amount of little slag particles was found in boiler L6, compared to the pure raw material. In boiler L5 no significant differences could be observed between those two fuels, and only little slag was found in both cases.

A quantitative evaluation of the slag formation tendency was done for the investigated fuels fired in boiler L8. In Figure 50 the amount of slag formed during combustion is compared, showing the fraction of slag particles in the residual ash considering the two largest particle fractions ($> 5.6 \text{ mm}$ and $5.6 \text{ mm} > x > 4 \text{ mm}$).

Adding bauxite, the amount of slag from straw combustion could be reduced by half, whereat the most relevant reduction was achieved for the fraction of largest particles ($> 5.6 \text{ mm}$). For maize whole crop as well a significant reduction was obtained through DollitTM addition, resulting in a total prevention of slag formation. However, contrary effects were observed

when applying the two additives to Miscanthus: Forming hardly any slag when burnt as pure raw material, the amount of slag in combustion residues was doubled, and even large slag particles were found. In Figure 51 pictures of the largest fraction of slag particles are shown for different fuels with and without additive.

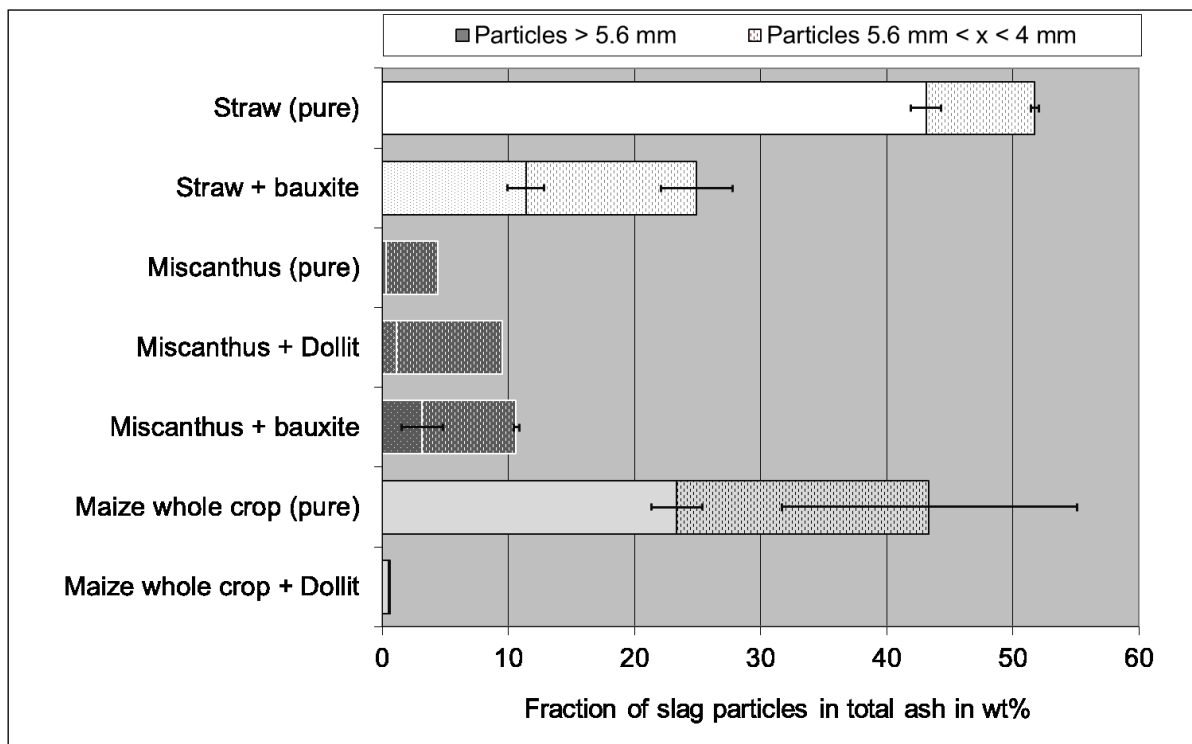


Figure 50: Slag formation of fuels with and without additives in boiler L8.

In agreement with the results from ash melting analyses in the laboratory, practical tests in real combustion appliances show that the use of Ca-, Mg- or Al-containing additives can improve ash melting properties, i.e. reduce the amount of slag or at least influence the nature of the agglomerates formed e.g. leading to rather porous and fragile than dense and molten structures.

Moreover, the results from the combustion of different Miscanthus samples show that the use of additives can also have a contrary effect, i.e. increase the slag formation tendency. This could be explained by a low-melting ash composition resulting from additive admixture which is not very likely since the effect was observed for both Ca- and Al-addition. Another explanation would be the high ash content caused by additives, that consequently leads to increased amounts of ash on the grate and thus facilitates the agglomeration of sticky or molten ash particles.



(a) Straw in L8



(b) Straw with bauxite in L8



(c) Miscanthus with Dollit™ in L8



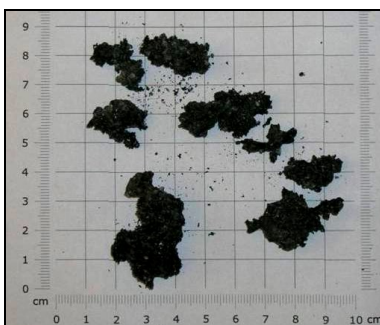
(d) Miscanthus with bauxite in L8



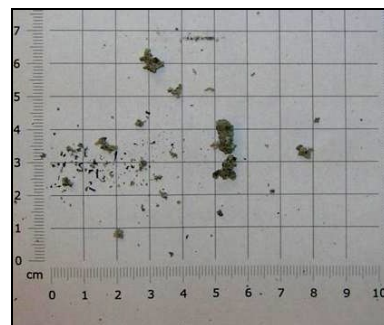
(e) Maize whole crop in L8



(f) Maize whole crop with Dollit™ in L8



(g) Maize whole crop in L6



(h) Maize whole crop with Dollit™ in L6

Figure 51: Fraction of largest slag particles after combustion of different fuels with and without additive. [CARVALHO 2007]

5.4.4 Discussion

Information gained from raw material classification

Characteristic melting temperatures and practical slagging behaviour of different biomass fuels were analysed. It was found that basic tendencies regarding ash melting properties may be estimated based on raw material classification according to ÖNORM EN 14961-1, however if any significant evaluation is only possible for a narrow and well-defined raw material basis like e.g. untreated wood residues without bark (classes 1.2.1.1 and 1.2.1.2) or straw parts from cereal crops (class 2.1.1.2).

Qualitative accordance for characteristic melting temperatures and practical slag formation was found for fuels assigned to both raw material classes i.e. HQ wood and straw: Softening temperatures for HQ wood were found to be relatively high with an average of 1390 °C and in a narrow range of fluctuation of 160 °C. Correspondingly, no slagging problems were observed in practical combustion tests for the fuels assigned to this fuel class. However, low SOT-values were measured for straw fuels, ranging from 726 °C – 840 °C, and all samples caused considerable slag formation during combustion.

High variability was found for characteristic melting temperatures as well as practical slagging behaviour among other fuel classes i.e. LQ wood (class 1.4), Miscanthus (class 2.1.2.1), grain (class 2.1.1.3) or hay (class 2.1.2.5). Fluctuation ranges of 330 °C – 490 °C were found for SOT-values. Moreover, considerable variations regarding the practical performance were observed for fuels assigned to the same class with some samples showing hardly any slag formation on one hand and severe slagging problems on the other hand.

All samples without information about source and origin of the raw material are summarized in the category of LQ wood. Therefore, both pellets made of bark-free stem wood and mixtures of all parts of a tree may be included, which explains well the high variability. Annual crops are usually more influenced by external factors such as soil conditions, fertilisation or harvest time when compared to wood (cf. section 3.3.1). Considerable influence of the above mentioned growing factors e.g. have been documented for Miscanthus (cf. LEWANDOWSKI 2003, CLIFTON-BROWN 2002). Moreover, raw material classes may comprise a number of different plants and species – e.g. genotypes of wheat and barley. Hay samples consist of a number of different herbs and grasses that vary seasonally. Thus, elemental composition and consequently ash melting properties can differ significantly for these fuels, and knowing the raw material source is not sufficient for an assessment of the ash melting behavior.

Relevance of property related classification with regard to ash melting behaviour and slag formation tendency

The classes determined via cluster analysis show similarities with regard to characteristic melting temperatures. Both SOT- and FT-values are found to be on a high level with a narrow fluctuation range for class 1, mainly consisting of HQ wood fuels. Also in class 2 fuels with relatively high characteristic temperatures are summarised, even though showing stronger variations. However, hardly any differentiation is possible between class no. 3, 4 and 5 in this regard, as temperatures are distributed over large intersecting bands, covering almost

identical value ranges. If anything, among these three classes No. 5 can be identified as the one covering fuels with the lowest melting temperatures.

More distinct characteristics were determined among the 5 classes when regarding the practical slag formation tendency, even though different combustion units had been applied. All investigated fuels that are either assigned to class 4 or 5 formed considerable amounts of slag during combustion, even in robust combustion appliances. Less severe but still significant slag formation could be observed for particular fuels in class 2 and 3, whereas for the major part of fuels in these classes no slag formation was observed.

Regarding the investigated wood fuels, both visual inspection of the PCA-plot and cluster analysis reflect the slag formation tendency in a good way. Fuels that formed slag in *Wood pellets test series I*, i.e. *LQ01*, *LQ02* and *HQ19*, are found clearly distant to the dense cluster of HQ wood fuels where no slag formation was observed, and *LQ02* is even assigned to class 2 instead of class 1 as all other samples of this test series are. Among the broad variety of fuels in *Wood pellets test series II*, severest slag formation and at the same time the largest distance to the cluster of HQ wood fuels in the PCA-score-plot is found for the samples *LQ15* and *LQ17*. Moreover, these two samples are even assigned to class 3 instead of class 2 where all other fuels of this test series are assigned. Also samples *LQ13*, *LQ18* and *LQ19* where little slag formation was observed in practical combustion tests show significant distance to objects representing non-slagging fuels.

Impact of type and nature of woody raw material

Slag formation problems when firing wood pellets are often related to the raw material basis. In order to find the most relevant factors, the impact of wood species, use of organic binders and raw material fraction in terms of bark, grinding dust, saw dust or wood shavings was investigated within *Wood pellets test series I*.

Among the investigated wood species, i.e. larch, pine and spruce, slag formation could only be observed for pellets made of 100 % larch when using unsoiled and bark-free stem wood of the respective species. Variations of fuel properties in terms of elemental composition and characteristic melting temperatures dependent on the type of wood were found to be low compared to the impact of bark addition or the range of variation determined for wood pellets made of unknown raw material investigated within *Wood pellets test series II*.

It was shown that the addition of bark considerably changes the elemental composition, by increasing the concentrations particularly of Al, Fe and Si, and consequently also the ash content. This is also reflected by the slag formation tendency, which is increased with increasing amounts of bark added. Similar results were found by ÖHMAN 2004 (1) and ÖHMAN 2004 (3) investigating pellets made of saw dust, logging residues and bark as well as a number of problematic and problem-free pellets from the market in residential burners. In contrast, no differences to pellets made of saw dust were observed when processing grinding dust or wood shavings.

Problematic wood pellets taken from the market also frequently showed increased concentrations of Al, Fe and Si, and usually also an increased ash content compared to own analyses of bark-free stem wood, which is in good accordance with findings by ÖHMAN 2004

(3). Some producers of these pellets also stated to process wood chips or bark in addition to sawdust (GRIESMAYR 2008). Moreover, strongly increased amounts of Si in some samples suggest contamination of the raw material e.g. with soil or sand (cf. LINDSTRÖM 2008). Therefore, the relevance of the type of wood is estimated to be low compared to the effect of impurities or the raw material fraction chosen.

The addition of up to 5 % of organic binders like shredded maize or rye flour was reflected in the elemental composition, mainly increasing the concentration of phosphorous. However, no significant changes with regard to ash content, characteristic melting temperatures or slag formation tendency could be observed for this amount of admixture.

Significance of elemental composition with regard to slag formation tendency

Regarding the elemental composition, some basic conditions that reduce or increase the probability of slag formation can be identified. In Table 30 trends regarding basic elemental composition and slagging propensity as reported in literature are summarized to simplified fuel categories.

Table 30: Simplified fuel categories as to their elemental composition

Trend of major ash constituents	Slagging propensity	Examples among the investigated fuels	Reference from literature
↓Si ↑Ca	Low	HQ wood fuels (spruce without bark)	Öhman 2004 (3), Lindström 2008
↑Si ↓Ca	Considerable/ increasing	wood with bark, larch, LQ wood pellets that formed slag	Öhman 2004 (3), Lindström 2008
↑Si ↑K	Severe	Straw, giant reed	Gilbe 2008 (1)
↑Si ↓K	Low	Miscanthus	Gilbe 2008 (1)
↑P ↑K	Considerable, reduced with ↑Ca	Wheat bran, maize whole crop	Lindström 2007

Fuels containing high fractions of Ca and hardly any Si (**↓Si↑Ca**) are usually non-slagging fuels, which was also observed for the investigated HQ wood samples of spruce without bark (cf. section 5.4.2.1). An increased slag formation tendency is expected with increasing fractions of Si and reduced amounts of Ca (**↑Si ↓Ca**) in the fuel ash. This trend could also be confirmed by the wood pellets with bark as well as the pellets made of 100 % larch, where increased fractions of K in addition to Si were determined. Moreover, the severest slagging samples among the LQ wood fuels showed considerably increased amounts of Si (cf. section 5.4.2.2), and also increased slag formation with increasing Si- and decreasing Ca-concentrations was observed for different hay pellets (cf. section 5.4.1).

Severe slag formation is attributed to high-Si fuels with considerable fractions of K (**↑Si ↑K**) [GILBE 2008 (1)], which is typically found for straw or grasses, and was also found for all investigated straw samples and also most hay samples as well as pellets made giant reed (cf. section 5.4.1). On the contrary, trouble-free operation and hardly any slag formation can be expected from high-Si fuels with at the same time low K-concentrations (**↑Si ↓K**) [GILBE 2008 (1)]. This was confirmed by the investigated Miscanthus samples, and in addition an increased slagging behavior with increasing K-concentrations could be observed for *MIp01* compared to *MIp02*.

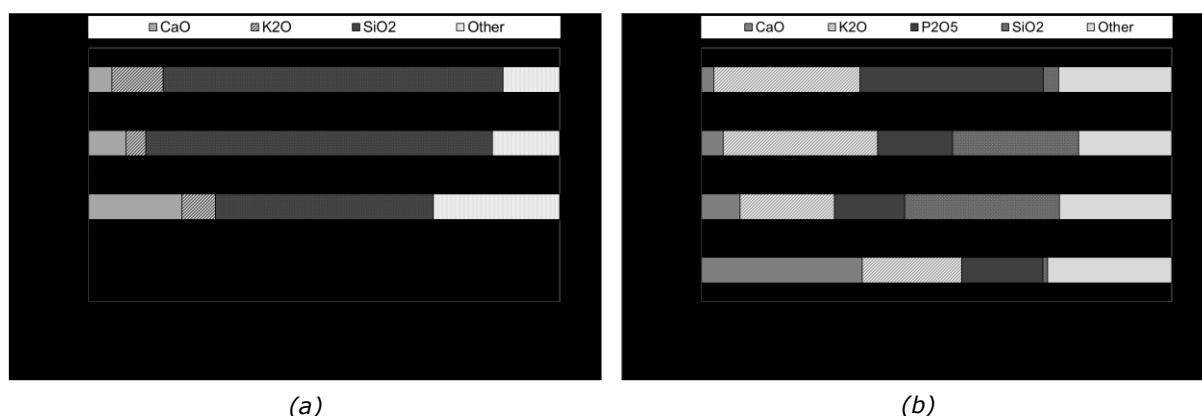


Figure 52: Elemental composition of the investigated Si-rich *Miscanthus* samples (MIp01, MIp02, MIp09) (a) and the P-rich fuels (wheat bran OTp03, maize whole crop MCp02 and MCp03, wood pellets with shredded maize HQ12) (b)

Among the P-rich fuels ($\uparrow P$), considerable slag formation was found for ash from wheat bran (OTp03), mainly consisting of P- and K-compounds. Moreover, slag was formed when burning pellets made of maize whole crop (MCp02, MCp03), showing also considerable amounts of Si in addition to P and K. However no slag was formed when burning wood pellets with 5 % shredded maize (HQ12), also showing relatively high concentrations of P, but no Si in the fuel ash. Thus, P-K- and P-K-Si-mixtures respectively show a high slagging potential, that can significantly be reduced by additional presence of Ca, which was also found by LINDSTRÖM 2007.

Apparently, not each fuel can be assigned to one of these prototype-categories, and often no characteristic differences can be detected regarding the composition of slagging and non-slagging fuels. Among the investigated LQ wood pellets e.g. no significant difference can be specified when comparing non-slagging fuel samples (i.e. LQ09, LQ10, LQ11 and LQ14) and pellets that formed some slag (i.e. LQ13, LQ18 and LQ19).

There are a number of compounds taking part in complex ash reactions, and even small amounts of particular elements can have a considerable impact on the ash melting properties. Therefore, no simple categories as to the slagging behavior can be defined based on the elemental composition. Detailed examination concerning more complex approaches in this regard is found in chapter 5.6.

Significance of ash content with regard to slag formation tendency

The ash content is often mentioned when discussing indicators or reasons for an increased slag formation tendency. In woody biomass higher ash contents are usually caused by adding other raw material fractions than bark-free stem wood – e.g. bark or branches – or may be due to soil contamination. Hence, a certain relation between ash content and slag formation intensity can be attributed to these fuels, as shown for the LQ wood samples investigated (cf. Figure 43). Regarding the whole range of biomass fuels, no correlation between ash content and slagging behavior can be verified (cf. *Comparison of fuel properties* in section 5.4.1 and 5.4.2.2). The elemental composition is the prevailing factor with regard to ash melting

properties, and differently to wood, no correlation is approvable between ash content and fuel composition for the variety of raw materials.

Significance of characteristic melting temperatures with regard to practical slag formation tendency

A vast set of reference data available in literature regarding characteristic melting temperatures of different biomass fuels. However, only little information is provided on both slag formation tendency of fuels in real combustion application and characteristic temperatures of these fuels respectively (cf. GILBE 2008 (2) and ÖHMAN 2004 (1)).

For the investigated samples of non-woody biomass fuels in section 5.4.1, a simple qualitative relation was found, where no or only very little slag formation was observed for fuels with a softening temperature (SOT) above 1000 °C, and an increased slag formation tendency was found for fuels showing lower SOT-values. However this relation is not applicable to the investigated wood pellets. Softening temperatures of all woody biomass fuels that formed slag clearly exceeded 1000 °C, and this is also true for the mixed biomass pellets investigated.

No differences with regard to characteristic melting temperatures are found comparing non-slugging HQ wood fuels and pellets that formed slag (i.e. made of 100 % larch or containing bark). An increasing slag formation tendency with decreasing flow temperatures (FT) was found for the investigated LQ wood pellets (cf. Figure 43 (b)). However, no such correlation could be detected for the softening temperature (SOT): In general SOT-values of the slugging fuels are slightly lower compared to the non-slugging pellets samples, but still temperatures of some slugging fuels are higher than those of particular non-slugging pellet samples. Moreover, no trend regarding the amount/severity of slag among the slag forming fuels could be detected.

Inconsistency is also found among the non-woody fuels. SOT-values of the three hay-samples (*HAp05*, *HAp06* and *HAp07*) are very similar unlike their considerably different slag formation performance in real combustion tests, and the highest flow temperature is found for *HAp07*, although this is the hay sample with the most distinct slag formation tendency.

Regarding the overassessment of characteristic temperatures, it can be assumed that the method of the ash fusion test is not suitable for all types of biomass, not being able to detect the melting onset for particular elemental compositions. Indication of initial ash reactions and melt formation below the IDT (according to ASTM D1857M) or SOT respectively have already been stated by numerous authors while using a variety of methods for means of comparison [e.g. WALL 1998, HANSEN 1999, BRYANT 2000, HJULER 2000]. In terms of the standard ash fusion test, it is assumed that the shape of the sample is maintained by a stable skeleton although initial melt has already formed, and thus the melting cannot be detected visually [HJULER 2000]. Consequently, characteristic melting temperatures would be determined too high. Furthermore, the formation of gas bubbles or expansion of the test specimen has been observed for coal but also straw ash samples [HJULER 2005, GUPTA 1998, WALL 1998], also complicating an accurate detection of the characteristic shape change. A comparably atypical characteristic was found for a number of straw samples with additive investigated in the present work (cf. section 5.4.3.1).

In contrast to overestimation of melting temperatures, also low slag formation tendency occasionally is observed for fuels showing relatively low SOT-values. Stable operation in spite of slag formation e.g. was possible using vine pruning pellets, despite their relatively low softening temperature of 795 °C. These inconsistency may be explained by a major impact of additional factors like e.g. residence time and ash melting reaction rate respectively.

If any, only a rough estimation of the slagging behavior may be provided by knowing the softening temperature (SOT). Due to large deviations to real slagging performance in particular cases, characteristic melting temperatures do not provide reliable and sufficient information in order to predict the slag formation tendency of a biomass fuel.

Properties and performance of raw material mixtures

Only two fuel samples of mixed biomass pellets have been investigated in order to gain basic knowledge regarding the properties of raw material mixtures. Therefore, 40 % corn cob residues (*Mx01*) and 10 % of straw (*Mx02*) respectively had been added to saw dust of bark-free spruce. Assuming homogeneous mixtures, ash content and elemental composition can be calculated according to the mixing ratio. However, characteristic melting temperatures and practical slag formation tendency need to be determined experimentally.

Severe slag formation was observed when burning the pellets containing straw, although only 10 % were added, keeping the ash content below 1 %. Less, but still considerable amounts of slag were found after the combustion of the mixed pellets with corn cob residues, despite the comparably high percentage of 40 % .

Although considerable slag formation was observed, high FT-values were determined for both fuel samples with > 1460 °C for *Mx01* and 1430 °C for *Mx02* respectively. Moreover, an unrealistic high softening temperature was measured for *Mx01* with 1400 °C, thus exceeding values typically measured for pure high-quality woody biomass.

Analysing the relation of slag formation tendency and ash content or characteristic melting temperatures, mixed biomass pellets show a different behavior when compared to LQ wood samples investigated within the same test series: The slag formation determined for mixed biomass pellets is considerably higher when compared to pure woody fuels with similar ash contents or melting temperatures (cf. Figure 43).

Effect of additives

It was found that both Al- and Ca-/Mg-containing additives can have a positive effect on the characteristic melting temperatures and the practical ash melting behavior of solid biomass fuels, and in general an improvement of the ash melting characteristic with increasing amounts of additive could be observed. This has already been documented by numerous authors (cf. section 3.3.5). Laboratory tests with straw pellets showed that softening temperatures in average could be increased by about 250 °C – 450 °C, and flow temperatures by 100 °C – 300 °C, dependent on type and concentration of the respective additive.

Similar results were found for Ca and Mg, and a stronger effect was observed when applying the same concentration of Al. Moreover, no impact of the type of chemical bonding in particular sulfates, carbonates or oxides was identified. However, accompanying elements like

e.g. Si or Fe change the elemental composition and consequently affect the ash melting properties.

Considerably improved melting properties as determined via ash fusion test could only be verified to some extent in practical combustion tests. Despite significantly increased melting temperatures, considerable amounts of slag were formed when firing straw with additive. However, the slag formation tendency of straw and maize whole crop was significantly reduced by using additives. A contrary effect was observed for *Miscanthus*: The addition of both DollitTM and bauxite slightly increased the amount of slag formed during combustion, whereas hardly any slag was formed when burning the pure raw material. In addition to changes regarding the elemental composition, also an increased ash content may be the reason for this behavior. Similar findings are also reported by ÖHMAN 2004 (2) where slag formation tendency of trouble-free wood pellets was increased by kaolin addition.

The resulting ash melting behavior depends on the properties of the mixture of additive and raw material, and thus the effect of one type of additive is not necessarily the same for different raw materials (which is also found e.g. by WANG 2014). Therefore, no general improvement strategy by using additives can be defined. Moreover, increased ash melting temperatures do not necessarily go along with improved practical ash melting behavior, as some samples show considerable slag formation despite high softening temperatures. Despite a potential positive effect, it has to be considered that additive utilization always goes along with an increase of the ash content.

5.5 Technology related aspects on slag formation

Different combustion units were tested with various biomass fuels in order to investigate technology related aspects on slag formation. Allowing for the different fuel properties, test series were conducted separately for woody and non-woody biomass fuels, using the most appropriate combustion technologies. In addition, combustion conditions in terms of air supply in the combustion zone as well as grate cleaning intervals were varied in selected units. In the following section, results and observations regarding slag formation are examined focusing on the design of the combustion zone, in particular fuel feeding, grate design and ash removal technology. Moreover, the relevance of air supply and grate cleaning settings is investigated.

5.5.1 Wood pellets fired in different combustion units

A number of specially made wood pellets were investigated in different combustion units as already described in section 5.4.2.1. These pellets were produced from different raw materials, including e.g. different wood species, bark fractions or organic binders like flour or starch, and still come up or slightly exceed requirements for class A1 pellets according to ÖNORM EN 14961-2. In addition, problematic fuel qualities obtained from the market were tested.

Combustion units were chosen in this way, to provide for variations with regard to fuel feeding, grate design and ash removal technology. Moreover, a pellet stove (unit L6) was investigated. The main characteristics of the selected boiler technologies are summarised in Table 31. In addition a qualitative description of slag formation and operating performance is provided for the pellets that formed slag.

Unit L1, L3 and L6 are topfeed systems with discrete ash discharge from the grate section. The grates in unit L1 and L6 are designed as pot and trough respectively, and combustion residues need to be transported through the grate openings. In contrast, in unit L3 this is done by opening the moving grate, thus being able to unblock the whole cross section area of the grate. Also discrete grate cleaning is applied in boiler L4 by opening the tilting grate, and in this unit the fuel is fed from the side. Boiler L5 is the only unit that continuously removes the combustion residues, which is effected by the fuel successively fed in the centre of the burner plate.

Temperatures in the fuel bed

Temperature measurement in the grate section or combustion zone is a difficult task, and it is a major challenge to define comparable measurement positions. However, it was found that typical temperatures in the fuel bed were comparable for almost all investigated units, ranging from 900 °C–1100 °C and even beyond. Only in boiler L5, the temperatures measured in the grate section and the fuel bed respectively were considerably lower, not exceeding 700 °C. This may be due to the open design, providing free space around the burner plate with some distance to the fire tube where temperatures are high due to gaseous combustion.

Performance of different combustion units

Most frequently, slag formation was observed in boiler L1. Severest slag formation was found for the pellets *LQ03* and *LQ05*, causing a shutdown of the boiler after 24 h of operation. The whole burner pot was filled with slag, forming one large tightly molten lump, thus inhibiting further combustion. This was also indicated by continuously increasing CO-emissions. Only little slag was formed during the combustion of *LQ01*, *LQ02* and *LQ08*, with a maximum size of slag lumps of about 0.5-1.0 cm. Moreover, considerable amounts of slag were found when firing pellets *HQ19*, but still separate lumps of 1-3 cm could be identified. Even though no disturbance of the combustion process due to this slight slag formation was observed during the 72 h combustion tests, problems are expected for permanent operation: Particles could not be removed from the burner pot through the perforated plate on the bottom and thus will gradually accumulate.

Table 31: Overview about the main characteristics of the different boiler/stove technologies and qualitative description of slag formation and operating performance for the pellets that formed slag.

Boiler ID	L1	L3	L4	L5	L6
Fuel feeding	↓ topfeed	↓ topfeed	→ from the side	↑ underfeed	↓ topfeed
Grate	Pot with per- forated plate on the bottom	Moving grate	Tilting grate	Burner plate	Grating
Ash removal system	Discrete, moving the perforated plate	Discrete	Discrete	Continuous	Discrete, manual cleaning
Typical temperatures in the fuel bed	900 °C – 1100 °C	940 °C – 1030 °C	Not measured	650 °C – 690 °C	850 °C – 1200 °C
LQ01	○ / ?	- / ☑	- / ☑	- / ☑	- / ☑
LQ02	○ / ?	- / ☑	- / ☑	- / ☑	○ / ☑
LQ03	●● / ☒	●● / ?	○ / ☑	● / ?	n.t.
LQ05	●● / ☒	● / ☑	n.t.	● / ☑	●● / ☒
LQ08	○ / ?	- / ☑	n.t.	n.t.	n.t.
HQ18	- / ☑	○ ^{#)} / ☑	- / ☑	- ^{*)} / ☑	- / ☑
HQ19	● / ?	- / ☑	○ / ☑	- ^{*)} / ☑	- / ☑
<div style="display: flex; justify-content: space-between;"> <div> <p>●●Severe slag formation</p> <p>●Considerable slag formation</p> <p>○Little slag formation</p> <p>-No slag formation observed</p> <p>n.t.....Not tested</p> </div> <div> <p>☑Trouble-free operation</p> <p>?(Trouble-free) operation possible, problems may occur with increasing operating duration</p> <p>☒Shutdown due to slag formation</p> </div> </div>					

^{*)} In one combustion unit little slag-type deposits were found on a thermocouple coverage. As long as no other slag formation was observed, the results were considered with “no slag”. Possibly an increased slag formation probability of the fuel can be assumed.

^{#)} power outage

In boiler L3 slag formation was only observed for high-slagging pellets *LQ03* and *LQ05*. The whole grate area was blocked with slag after 24 h of operation with *LQ03*, and the slag

formed could not be removed by opening the moving grate. Even though no impact on the combustion quality was observed during this 24 h experiment, problems are expected for continuous operation as the combustion zone will be blocked by slag shortly. Also considerable amounts of slag were found when firing pellets *LQ05*, but slag lumps were discharged by the moving grate. Therefore, trouble-free operation may be possible in this case.

In boiler L4, slag was formed when firing pellets *LQ03* and *HQ19*, and resulting agglomerates were comparably little and small. Moreover, all slag formed was removed when operating the tilting grate, so that unimpaired long-term operation is assumed.

In boiler L5 slag was formed for pellets *LQ03* and *LQ05*. A ring-shaped slag lump was formed on the burner plate when firing pellets *LQ03*. Despite molten structures could be identified, the slag lump was easily breakable on manipulation. However, trouble-free continuous operation might be problematic: Further growth and hardening of the slag ring seems likely, thus impeding ash removal and consequently blocking the combustion zone. Ash from the combustion of pellets *LQ05* only formed small slag lumps (maximum size of 1 cm) that were easily discharged from the burner plate by the successive fuel, thus facilitating trouble-free permanent operation.

Smallest slag particles were found in the grating of the pellet stove (unit L6) after the combustion of *LQ02*, showing no impact on the combustion process during the 7h-combustion test. A satisfactory operation of the stove with this fuel seems feasible with manual cleaning in regular intervals assumed. Slag formed from pellets *LQ05* completely filled the grating after 7h operation, resulting in one large hard slag lump that inhibited further combustion.

Description of slag formed

Considerable differences are observed with regard to size and consistency of slag lumps formed when using the same fuel in different combustion units. An overview about slag samples from selected wood fuels is provided in Table 32.

Largest slag agglomerates or even only one big slag lump are formed in the units L1, L3 and L6. No agitation of the fuel bed during combustion is provided due to the grate design of these units, in particular L1 and L6 which are designed as burner pot and trough-shaped grating respectively.

Comparably small and more loose structures are formed in boiler L5 where fuel and combustion residues are transported continuously over the burner plate, starting with fuel feeding in the center and discharging ash and slag on the edge of the plate. Therefore, residence time of combustion residues in the hot part of the fuel bed is short when compared to systems with discrete grate cleaning technology. Moreover the size of the grate may have an impact on the characteristics of the slag formed, bringing about more or less contact among the ash and slag particles respectively.

Little amounts of slag formed in boiler L4 may additionally be explained by different combustion conditions (e.g. temperatures in the fuel bed). Of course, design of the grate or the combustion zone is not the only relevant factor regarding technology related aspects on slag formation. Prevailing temperature- and gas phase conditions also impact the slag forming

reactions, and results cannot only be attributed to one of these interacting factors. However, design aspects play important role among prerequisites and reasons provoking slag formation.

Table 32: Slag samples from selected wood fuels formed in different combustion units.
(Pictures: FRIEDL 2006)

	L1	L3	L4	L5	L6
LQ02		No slag	No slag	No slag	
LQ03					Not tested
LQ05			Not tested		
HQ19		No slag		No slag	No slag

5.5.2 Different types of boilers tested with non-woody biomass fuels

Several non-woody biomass pellets were fired in different combustion units as already described in the sections 5.4.1 and 5.4.3.2. In order to consider a wide range of fuel properties different raw materials have been chosen, i.e. straw, Miscanthus and maize whole crop. Moreover, pellets with and without additives were tested.

Adaption measures

Combustion tests were conducted in state-of-the-art combustion units. However, slight adaptations were necessary in order to enable stable combustion over a period of several hours with all fuels tested.

Boiler L5: The size of the burner plate was reduced by almost 14 %, and the fire tube was raised by 25 mm in order to provide more space for the slag particles to be discharged.

Boiler L7: The size of the burner plate was reduced by 50 % in order to provide more space for the slag lumps to be discharged.

Boiler L8: A kind of agitator was installed at the edge of the moving grate in order to break of large parts of slag. Moreover, the frequency of regular grate movements was increased to avoid ash and slag accumulation on the grate.

The main characteristics of the selected boiler technologies are summarised in Table 33. In addition a qualitative description of slag formation and operating performance is provided for all investigated pellets. Apart from the aspects considered in this table, the impact of atmosphere in the grate section cannot be quantified.

Table 33: Overview about the main characteristics of the different boiler technologies and qualitative description of slag formation and operating performance for the investigated pellets.

Boiler ID		L5	L6	L7 I	L7 II	L8
Fuel feeding		↑ underfeed	↓ topfeed	↑ underfeed	↑ underfeed	→ from the side
Grate		Burner plate	Grating	Burner plate	Burner plate	Moving grate
Ash removal system		Continuous transport	Discrete manual cleaning	Continuous transport	Continuous transport	Regular grate movements + slag scraper
Typical temperatures in the fuel bed		Measured values vary considerably due to slag formation in the measurement zone. Therefore, values of particular tests are compared if necessary. Moreover, values from reference tests with wood can be used for means of comparison.				
Fuel ID						
Straw	STp01	●● / ☒ ~17h	●● / ☒	●● / ☒ 4h	●● / ☒ 15h	n.t.
	STa02	●● / ☒ ~17h	●● / ☒	● / ☒ 4h	● / ☒ 15h	n.t.
	STa03	● / ?	● / ☒	● / ☒ 4h	● / ☒ 20h	n.t.
	STp03	n.t.	● / ☒	n.t.	n.t.	●● / ?
	STa06	n.t.	● / ☒	n.t.	n.t.	● / ?
Miscanthus	MIp01	n.t.	● / ☒	● / ☒ 5h	● / ☒ 6h	n.t.
	MIp02	- / ☒	- / ☒	n.t.	n.t.	- / ☒
	MIa01	- / ☒	○ / ☒	n.t.	n.t.	○ / ☒
	MIa02	n.t.	○ / ☒	n.t.	n.t.	○ / ☒
Maize w.c.	MCp02	○ / ☒	- / ?	● / ☒ 9h	○ / ☒	n.t.
	MCp03	○ / ☒	● / ☒	n.t.	n.t.	● / ☒
	MCA05	○ / ☒	○ / ☒	n.t.	n.t.	- / ☒
<div>●●.....Severe slag formation</div> <div>●Considerable slag formation</div> <div>○Little slag formation</div> <div>-No slag formation observed</div> <div>n.t.....Not tested</div> <div>☒Trouble-free operation</div> <div>?(Trouble-free) operation possible, problems may occur with increasing operating duration</div> <div>☒Shutdown due to slag formation</div>						

Performance of different combustion units

In general, all investigated fuels showed a high slag formation tendency when compared to wood, and considerable differences were observed dependent on the type of raw material. Nevertheless, significant differences regarding the combustion performance are found among the investigated technologies.

For fuels with a low slag formation tendency the combustion technology can be the crucial factor, deciding whether slag is formed or not. The performance of combustion units operated with these fuels can range from “trouble-free permanent operation” to “shut-down after several hours due to slag formation”. For such fuels a major impact of combustion conditions in terms of temperature, atmosphere or residence time is assumed.

Miscanthus with DollitTM (*MIa01*) e.g. formed smallest slag lumps of a few millimeters when burned in unit L6 and L8, whereas no slag was found after the combustion in boiler L5. One reason for this could be very low temperatures on the burner plate of boiler L5, reaching only 350 °C – 500 °C in this experiment, whereas 650 °C – 800 °C were measured in the fuel bed of boiler L8. Even though no data about fuel bed temperatures are available for unit L6, temperatures are also assumed to be higher, referring to previous experiments [FRIEDL 2006].

Different slagging performance was also found for maize whole crop with additive (*MCa05*), with little slag particles formed in unit L5 and L6, and no slag formation in boiler L8.

Considerable differences were observed when burning pure maize whole crop (*MCp02*): Even though no slag formation was observed in unit L6, the ash could not be removed appropriately, leading to overfilling of the grating. However, slag was found in boiler L5 as well as boiler L7 (I and II) when burning *MCp02*. More severe slagging was observed for the original design of boiler L7 (I) compared to the adapted version (II), showing slag lumps that were larger and highly molten, even leading to malfunction of the boiler after 9 hours of operation. Pictures of the grate section of the respective units as well as slag samples of boiler L7 I and L7 II are shown in Figure 53. Temperatures in the fuel bed are slightly lower in unit L5 with about 510 °C – 590 °C compared to L7 I and L7 II with average values of 680 °C and 730 °C respectively. However, transport and removal of combustion residues are estimated to be crucial in this case. Sufficient space is provided in both boiler L5 and boiler L7 II to discharge ash and also slag lumps formed. On the contrary, only little space is provided to remove the combustion residues in unit L7 I, additionally leading to a longer residence time of ash and slag on the grate.

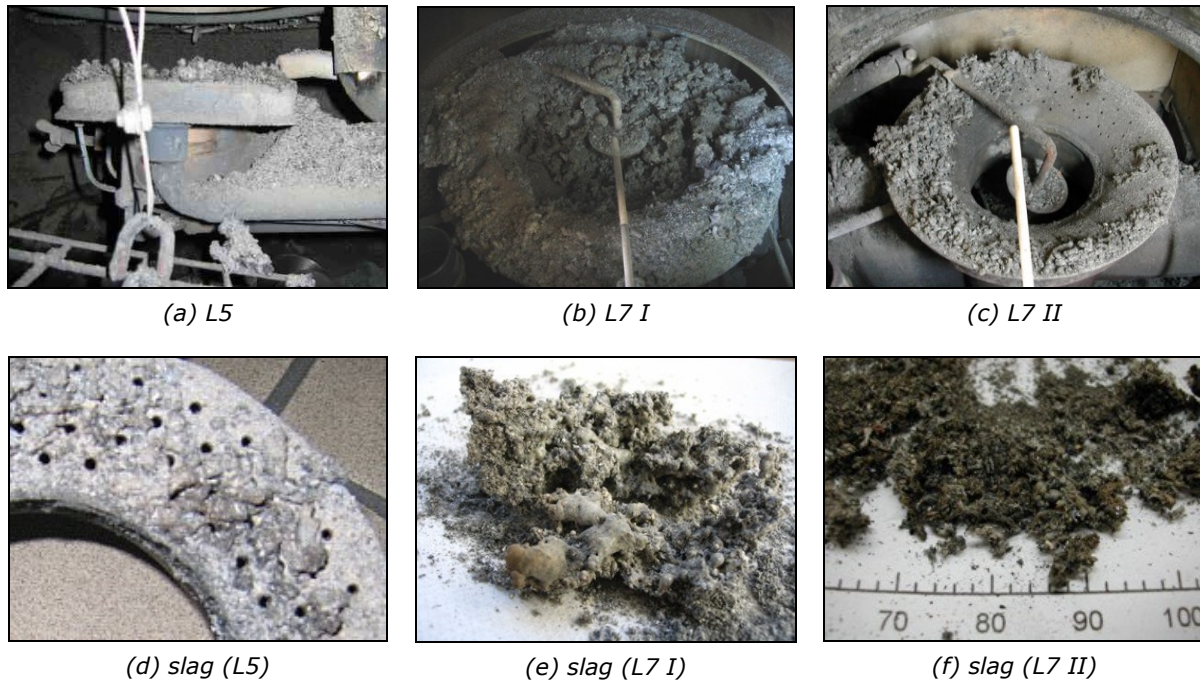


Figure 53: Grate section of boiler L5 (a), L7 I (b) and L7 II (c) and slag formed in the respective boilers ((d) - (f)) after the combustion of MCp02. [CARVALHO 2007]

However, as most non-woody biomass fuels tend to form slag, the core issue is how combustion units cope with these fuels and the slag formed respectively. Slag was formed in all experiments with MCp03. Whereas unit L6 had to be shut down after a few hours, permanent operation seemed possible when applied in unit L5 and L8 respectively, where ash and slag could be removed appropriately.

Severe slag formation was observed in all investigated combustion units when burning straw fuels. Therefore, the performance was assessed by comparing how long the respective units could be operated until being shut down. Only about 1 hour of operation was possible in unit L6, and for boiler L7 I operating performance was acceptable for about 4-5 hours. Considerably longer operating duration was achieved for the same fuels when burned in unit L5 and L7 II, providing more space for ash removal. Compared to all other investigated units, no shutdown occurred when firing straw in boiler L8, being the only technology with an active ash removal system.

5.5.3 Air supply in the combustion zone

The amount of primary air as well as the position of the air inlet influence temperature, flow conditions and gas chemistry in terms of oxidising or reducing species in the grate section. As ash melting reactions are strongly dependent on these parameters, the effect of air supply on slag formation was investigated.

In addition to experiments using standard settings, wood pellets tests in boiler L3 were conducted with reduced aeration by cutting off the primary air supply (PAS). In Table 34 a qualitative evaluation of the slagging performance is given for different wood pellets in boiler L3 operated using original settings as well as reduced primary air supply.

Table 34: Performance of the investigated wood pellets fired in boiler L3 with original settings and reduced primary air supply (PAS shut).

	LQ01	LQ02	HQ07	HQ12	HQ15	HQ18	HQ19
Original	- / <input checked="" type="checkbox"/>	- / <input checked="" type="checkbox"/>	- / <input checked="" type="checkbox"/>	- / <input checked="" type="checkbox"/>	- / <input checked="" type="checkbox"/>	○ ^{#)} / <input checked="" type="checkbox"/>	- / <input checked="" type="checkbox"/>
PAS shut	- / <input checked="" type="checkbox"/>	● / ?	- / <input checked="" type="checkbox"/>	- / <input checked="" type="checkbox"/>	- / <input checked="" type="checkbox"/>	○ / <input checked="" type="checkbox"/>	- / <input checked="" type="checkbox"/>
	Significant ash caking	Slag, severe ash caking	Slight ash caking	Slight ash caking	Slight ash caking	Slag, severe ash caking	Slight ash caking, larger agglomerates
●.....severe slag formation			<input checked="" type="checkbox"/>Trouble-free operation				
●considerable slag formation			?(Trouble-free) operation possible, problems may occur with increasing operating duration				
○little slag formation							
-no slag formation observed			<input checked="" type="checkbox"/>Shutdown due to slag formation				

^{#)} power outage

Compared to original boiler settings, slag formation and severe ash caking respectively were observed for particular fuel samples when cutting off the primary air supply.

For almost all investigated fuels, at least small slightly sintered ash agglomerates that were easily breakable on touch were found in the ash box under the grate, when operating the boiler with reduced primary air supply. Moreover, slight ash caking in the grate section was observed for almost all fuels. However, bigger ash agglomerates were found after the combustion of pellets made of larch (HQ19) applying the same conditions. Severe ash caking was observed for pellets made of pine (HQ18) and spruce with 5 % bark addition (LQ02), and significant ash caking was also found for LQ01 (spruce with 2 % bark addition). The sintered structures accumulated in the grate section and could not be removed even if the moving grate was completely opened. For LQ02 and HQ18 even molten slag structures were found among the combustion residues. Figure 54 shows a bottom view of the grate area of boiler L3, with the moving grate completely opened. The pictures show ash caking after combustion of LQ02 (a) and HQ18 (b) when fired without primary air supply. For means of comparison, also the situation after combustion of HQ18 using original boiler settings is shown, where no ash caking was observed.

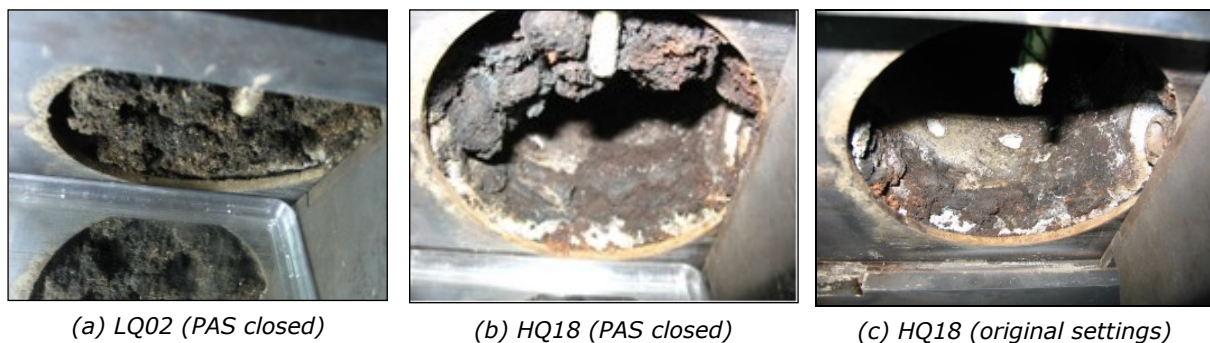
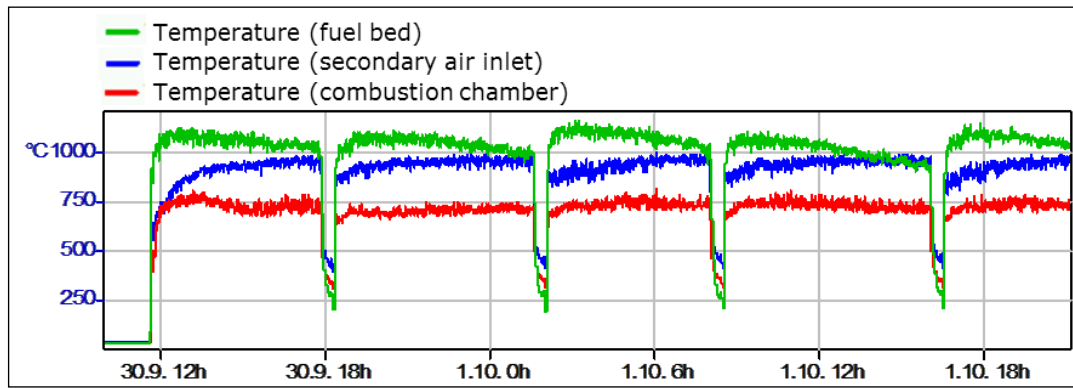


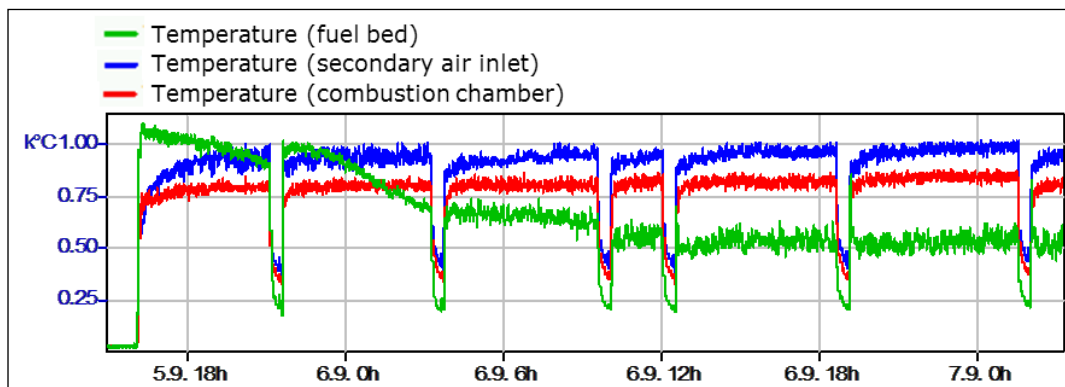
Figure 54: Bottom view of the grate area of boiler L3 with moving grate completely opened. (Pictures: FRIEDL 2006)

It is assumed that the turbulence in the grate area of the combustion zone was considerably reduced by cutting off the primary air supply, facilitating sintering of the ash accumulating in the grate section. Dependent on the fuel quality, the so formed agglomerates are either

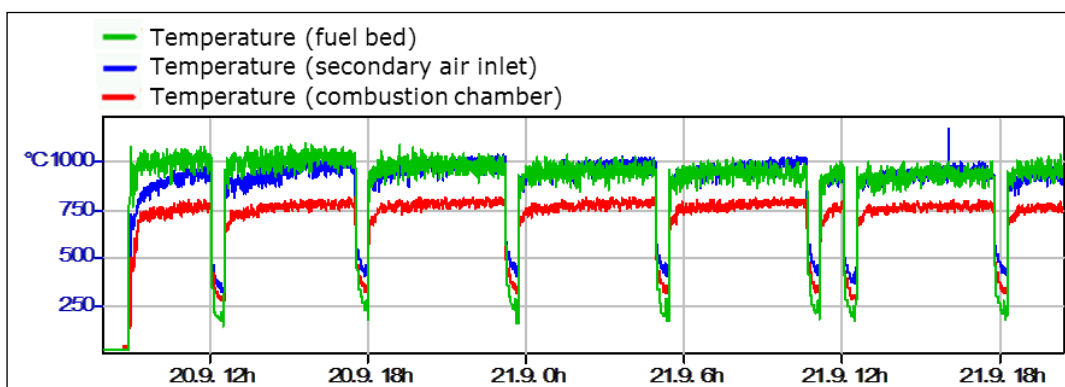
discharged by opening the moving grate, or remain in the grate section e.g. due to increased stickiness or bridging effects. Consequently the residence time of ash on the grate was considerably increased, thus also increasing the probability of ash melting and slag formation. This theory is also supported when looking at the progression of the fuel bed temperature in the course of a combustion test. In Figure 55, temperatures measured in the combustion section are presented for combustion tests without primary air supply for pellets *LQ02* and *HQ19*, and *LQ02* using original boiler settings.



(c) HQ19 – PAS closed



(b) LQ02 – PAS closed



(c) LQ02 – original settings

Figure 55: Temperatures in the combustion zone for the first 36 hours of the combustion test in boiler L3.

A continuous decrease of the fuel bed temperature is observed for the tests without primary air supply, which is most probably due to the ash accumulating in that section. Only a minor decrease is observed for pellets *HQ19*, and the initial temperature is achieved again after each grate cleaning procedure. However, a stronger decrease of the fuel bed temperature is observed when burning pellets *LQ02*, and this trend is continued in spite of regular grate cleaning, representing agglomerates and ash caking that cannot be removed from that section. For means of comparison, temperatures are also shown for the same fuel when burned using original boiler settings (cf. Figure 55 (c)), where comparably stable values are measured during the whole experiment.

The combustion performance is not necessarily impacted by ash caking, unless agglomerates become as large that they cannot be discharged any more and affect the combustion quality.

5.5.4 Agitation of the fuel bed and grate cleaning intervals

Varying the frequency of the moving grate in boiler L8

Preliminary adaptations of boiler L8 were conducted aiming at a trouble-free operation for a minimum test period of 8 h with non-woody biomass fuels. Thus, the main issue was to optimize ash and slag discharge by varying the settings of the moving grate. Therefore, the frequency of grate movements was successively increased and tested with non-woody fuels in each case. Straw and Miscanthus were chosen, representing a low-ash and a high-ash quality among the non-woody raw materials.

Large agglomerates of slag were formed at low grate cleaning frequencies, blocking the ash discharge and thus leading to ash and slag accumulation in the combustion chamber and consequently to a shutdown of the unit. Moreover CO-emissions increased due to worsened conditions in the combustion zone. It was found that the combustion performance of straw could significantly be improved by increasing the grate cleaning intervals. However, the limitation in this regard was that from a certain frequency on no stable fuel bed could be established any more. This was also observed for Miscanthus, already at a lower frequency most probably due to the lower ash content accordingly. An overview about the combustion performance of straw and Miscanthus at different grate cleaning settings is provided in Table 35.

Table 35: Combustion performance of straw and Miscanthus in boiler L8 using different grate cleaning settings.

Frequency of grate cleaning	300	150	100	60	40	20
Straw (STp01)	☒ Shutdown after 3 h, slag blocked the combustion chamber	☒ Shutdown after 6 h, slag lump blocked moving grate	☑	☑	☑	☒ No stable fuel bed could be established
Miscanthus (MIp02)	n.t.	n.t.	n.t.	☑	☒ No stable fuel bed could be established	n.t.
☑ Stable operation for at least 8 h possible n.t. Not tested ☒ No stable operation for 8 h						

In addition to the qualitative evaluation in the course of preliminary tests, slag formed at different grate cleaning conditions was also assessed quantitatively. In Figure 56 the fraction of slag agglomerates (> 5.6 mm) in total ash from the combustion of straw using different grate cleaning frequencies is shown. It was found that the amount of these large agglomerates was significantly reduced by increasing the frequency of grate movements. Moreover, comparable results are found for different tests conducted under the same conditions.

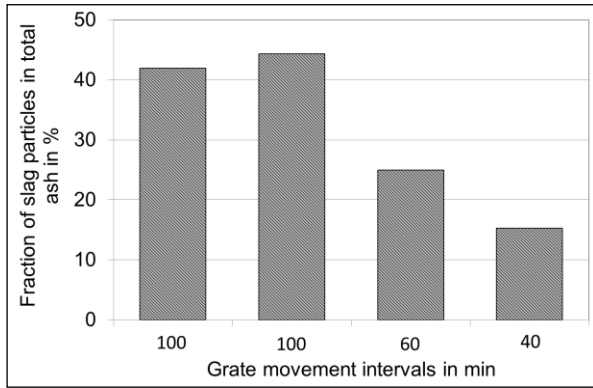


Figure 56: Fraction of slag agglomerates > 5.6 mm in total ash from the combustion of straw (STp03) applying different grate cleaning frequencies. (adapted from WOPIENKA 2007)

Impact of different grate cleaning intervals in boiler L2

Tests with different wood pellet qualities were conducted in boiler L2 as already described in section 5.4.2.2. The grate in boiler L2 is designed as a perforated plate, where holes can be opened by twisting a second plate mounted below, in order to discharge combustion residues. This is done every 6 hours according to the standard settings, not expecting any slag formation when using class A1 pellets. Assuming an increased slagging propensity for the investigated pellets qualities, additional settings with a higher grate cleaning frequency were defined, and consequently intervals were reduced to 200 min., 140 min. and 80 min. respectively.

Considerable differences were found dependent on the respective grate cleaning intervals. The fraction of slag that remained in the burner pot after 6 hours of operation is presented in Figure 57 for all fuels that showed slag formation in at least one of the 4 different test settings.

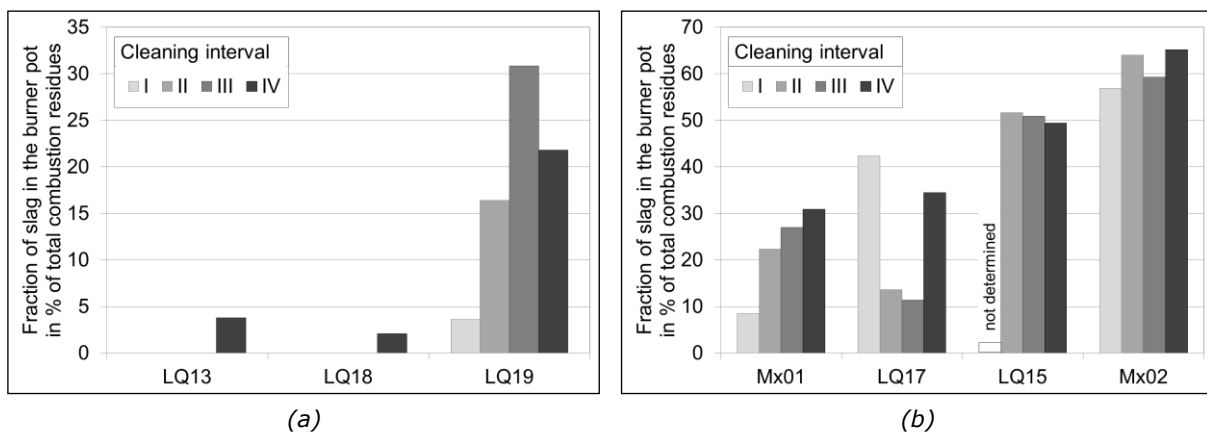


Figure 57: Fraction of slag that remained in the burner pot after 6 h of combustion when applying different grate cleaning intervals, i.e. 80 min. (I), 140 min. (II), 200 min. (III) and 360 min. (IV). Results are shown for fuels with minor slag formation tendency (a) and fuels that showed severe slag formation (b).

For LQ13 and LQ18 slag formation was only observed if no additional cleaning within the experimental period of 6 hours was conducted. For most of the other slag forming fuels, a tendency was found showing higher fractions of slag remaining in the burner pot with decreasing grate cleaning frequency. However, not all fuels absolutely follow this trend, and in

particular for severe slagging fuels, similar results are found for all 4 intervals. In these cases, slag formation is that severe, that no influence and improvement respectively by more frequent grate cleaning can be achieved.

5.5.5 Discussion

Combustion tests have been conducted applying several woody and non-woody biomass fuels to different small-scale combustion technologies. Results and findings regarding technology related influencing factors on slag formation are summarised and discussed in the following section, highlighting the following aspects:

- Design of grate area and ash removal zone
- Agitation of the fuel bed
- Residence time and ash removal solution
- Fuel flexibility

However, influencing factors cannot be discussed completely independent as they are often interrelated.

Design of grate area and ash removal zone

Usually, malfunction or shut-down of a unit is caused by accumulation of ash- or slag-lumps in the combustion zone, initially bringing about worsened combustion conditions, followed by blocking grate section and consequently the supply with fresh fuel, and finally leading to a shutdown of the unit. Therefore, the main challenge is to enable a consistent transport and discharge of ash and slag through the combustion zone, thus providing for appropriate combustion conditions.

Pot-type or trough-shaped grate systems, where ash needs to be discharged through a kind of grid were found to be inappropriate for slag forming fuels. The worst performance among all units tested with woody fuels was observed for unit L1: Even small slag particles could not be removed and thus are expected to accumulate with longer operating duration, and more severe slagging fuels formed one big lump of slag, filling the whole burner pot. Similar results were found for unit L6. Comparable results are reported by ÖHMAN 2004 (2) where most severe slag formation among three combustion technologies was found for over-feeding system.

In boiler L5 as well as boiler L7 combustion residues are transported from the centre to the edge of the burner plate where they are discharged to the ash box. In both units, the cross-section dimension of the burner plate was reduced, and additionally the fire tube was raised in boiler L5 in order to provide more space for the slag particles to be discharged. Thereby, an improved performance was observed for both units when operated with high-slagging fuels.

Considerable agglomerates were removed from the grate of boiler L3 by opening the moving grate. Moreover, slag lumps of several centimetres could be discharged from the grate of boiler L8, where the opening to the ash box was regularly increased by shifting the moving grate.

Also, a certain impact of the grate area design with regard to fuel bed temperatures was found: Significantly lower temperatures measured for boiler L5 are attributed to the open design of the grate section, providing free space around the burner plate with some distance to the fire tube where high temperatures are prevailing due to gaseous combustion. Consequently, less molten or smaller slag lumps were formed from particular fuels like e.g. fuel *LQ03*, *LQ05* or *MIa01*, when compared to other technologies.

As a result, sufficient space is required on the grate, also avoiding any constructive barriers or dead zones. Moreover, an adequate size is required for ash discharge openings in order to enable the passage of slag or agglomerates formed. Moving or tilting grates are advantageous in this regard, being capable of providing large openings up to the whole cross-section of the grate.

Agitation of the fuel bed

Continuous transport of fuel and ash through the combustion zone at the same time means continuous movement of the fuel bed. More vigorous agitation of the fuel bed can be managed by applying a moving grate.

Among the combustion units tested with woody fuels, boiler L5 was the only technology with continuous transport of fuel and ash respectively, thus providing regular agitation of the fuel bed. The slag lumps formed were comparably small and good operation performance was observed when compared to the other technologies tested.

Units with continuous fuel and ash transport were chosen for tests with non-woody biomass fuels, disregarding unit L6. It is therefore considered as basic requirement for trouble-free boiler operation with high-ash and even more high-slagging biomass fuels. Additional regular shifts of the moving grate turned out to be advantageous in boiler L8, in general showing the best capability in handling large amounts of slag.

Also, aeration in the grate section can bring about some movement to the fuel bed. Increased ash caking and also slag formation were observed when cutting off the primary air supply in boiler L3. Due to the long residence time of ash without any agitation, ash particles were sintered to agglomerates that stuck to the combustion chamber material in some cases, thus blocking the ash discharge.

Of course the influencing factors cannot be discussed independently as they are often interrelated. However, regular movements of the grate with sufficient space seem to reduce the risk of ash caking on the boiler material. Moreover, rather separate slag lumps are formed instead of one large agglomerate when providing for appropriate agitation of the fuel bed.

Residence time and ash removal solution

Apart from ash and slag accumulation, continuous ash removal or discrete grate cleaning intervals determine the residence time of combustion residues on the grate. In this regard, combustion technologies with continuous ash discharge seem advantageous compared to discrete ash removal solutions, where much more time is available for sintering and melting reactions. Also the size of the grate is important as to the aspect of residence time: Apart from widening the passage for ash removal, the shortening of the burner plate of unit L5 and

L7 also resulted in a reduction of the residence time in the combustion zone by reducing the distance between fuel feeding and ash discharge.

It was shown that trouble-free permanent operation is possible in spite of slag formation as long as agglomerates formed are regularly removed, and it has previously been discussed that basic requirements in this regard are the formation of separate removable ash lumps as well as sufficient space in order to discharge them. However, in some tests with boiler L5 and boiler L7, ring-type slag agglomerates were formed on the burner plates. The driving force of the successive fuel was not sufficient to remove these slag barriers, and blockage due to slag accumulation on the burner plate is assumed with increasing operating duration. In this case, an active ash transport by using cleaning tools or moving the grate or parts of the grate would be required, in order to enable a complete discharge of combustion residues.

Variation of the cleaning intervals of the moving grate in boiler L8 showed that the formation of large slag lumps is reduced and thus operating performance is improved by increasing the grate cleaning frequency. However, a certain residence time and grate load respectively is required in order to ensure stable combustion conditions and a complete burnout.

Fuel flexibility

Tests aiming at an optimisation of the grate cleaning intervals in unit L8 showed different results for the combustion of straw and Miscanthus. It can be concluded that appropriate settings vary dependent on the fuel properties, in particular the ash content. Therefore, different grate cleaning intervals and eventually also different grate areas are required, in order to avoid overload and consequently increased slag formation probability.

Requirements for combustion appliances suited for slagging fuels

Based on the findings regarding technology related influencing factors on slag formation, requirements were identified in order to enable trouble-free operation small-scale combustion units using slag forming fuels. Basic measures in this regard are summarised in Table 36 below.

Table 36: Problems and respective measures for the design of combustion technologies suited for slagging fuels

Measure	Problem	Example
Facilitate ash discharge Avoid constructive dead zones, bottlenecks and barriers	Ash accumulation , bridging, ash caking	Unobstructed ash removal zone sloping grate or curved burner plate,...
Reduce (ash) load of the grate Reduce the size of slag lumps	Formation of large slag lumps, seizing of slag lumps	Ample dimensioning of the grate section, mechanism to crush slag lumps (e.g. slag scraper)
Regular agitation of the fuelbed	Ash caking, formation of large slag lumps	Regular grate movements, continuous ash transport / ash discharge,
Optimisation of residence time	Extensive fusion of ash particles	Variable grate cleaning intervals or variable grate dimensions

Table 36 (continuation): Problems and respective measures for the design of combustion technologies suited for slagging fuels

Measure	Problem	Example
Sufficient space / wide openings for ash discharge	Retention of slag lumps	Ample dimensioning of the grate section, avoiding ash/slag transport <u>through</u> the grate
Active ash transport and discharge	Ash/slag accumulation, formation of large slag lumps and barriers	mechanism to crush or push slag lumps (e.g. slag scraper)
Flexibility of boiler settings as to particular fuel properties	Different requirements dependent on varying fuel properties	Variable grate cleaning intervals or variable grate dimensions

5.6 Theoretical approaches to determine the ash melting behaviour

Complex reactions take place in ash and slag formation, and even small changes of the composition can significantly influence the ash properties. Numerous approaches can be found in literature where slagging or ash melting characteristics of fuels or the respective ashes are evaluated based on the elemental composition. Indices or critical numbers are calculated from elemental concentrations which are considered as mainly relevant for the particular problem. Apart from indices providing qualitative information, also concrete values for characteristic ash melting temperatures are calculated based on empirical correlations.

In this chapter available correlations are applied to own biomass data in order to evaluate their relevance with regard to the evaluation of ash melting properties and slag formation propensity of solid biomass fuels. In addition, the results are considered for the development of a new calibration model.

5.6.1 Applicability of available equations to own biomass data

The most significant indices and equations were selected from the overview in chapter 3.4.1 in order to be applied to own biomass data. In Table 37 and Table 38 the selected calculation methods are summarised.

Table 37: Overview about elemental indices selected to be applied to own data set

Description of approach	Result	Developed for	Reference
Sum of basic oxides: $\Sigma = Fe_2O_3 + CaO + MgO + K_2O + Na_2O$	qualitative, varying with Si/Al ratio	Coal	BRYERS 1996
Base/Acid ratio: $R_{b/a} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + TiO_2 + Al_2O_3}$	qualitative, varying with Si/Al ratio	Coal	JENKINS 1998, STOIFL 2000, PRONOBIS 2005
Base/Acid ratio (including phosphorous): $B / A_{(+P)} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O + (P_2O_5)}{SiO_2 + TiO_2 + Al_2O_3}$	qualitative	Coal, derived for biomass	PRONOBIS 2005
Silica-ratio (slag viscosity index): $S_R = \frac{SiO_2 \cdot 100}{SiO_2 + Fe_2O_3 + CaO + MgO}$	qualitative	Coal	PRONOBIS 2005, NICHOLLS 1940
Elemental molar ratio: $\frac{Si}{Ca + Mg}$	qualitative	Biomass	LINDSTRÖM 2008
Elemental molar ratio: $\frac{Si + K + P}{Ca + Mg}$	Qualitative	Biomass (phosphorous- rich)	SOMMERSACHER 2011

The fraction of basic oxides has frequently been reported as crucial factor, and this term is also included in numerous equations (cf. BRYERS 1996 and REISINGER 1993). Calculating the base/acid-ratio $R_{b/a}$, the sum of basic oxides is additionally related to the sum of acid oxides.

PRONOBIS 2005 suggests that for biomass fuels additionally the fraction of P_2O_5 should be considered in this number ($B/A_{(+P)}$). Moreover, the slag viscosity index [PRONOBIS 2005] and the elemental ratio of $Si/(Ca+Mg)$ according to LINDSTRÖM 2008 are investigated.

In addition to fuel indices, five equations were chosen that have been developed to calculate characteristic melting temperatures of fuel ashes, i.e. softening temperature and flow temperature.

Table 38: Overview about empirical equations selected to be applied to own data set

Formula(s)	Result	Developed for	Reference
$SOT_{red} = 2863 - 37 \cdot \Sigma + 0.151 \cdot \Sigma^2, Si / Al \gg 1$ $SOT_{red} = 2992 - 27.1 \cdot \Sigma + 0.27 \cdot \Sigma^2, Si / Al \approx 1$ $\Sigma = Fe_2O_3 + CaO + MgO + Na_2O + K_2O$	SOT ^{+))}	Coal	BRYERS 1976
$SOT = 1094 + 42.5 \cdot K_{fu}$ $FT = 1139 + 48.6 \cdot K_{fu}$ with $K_{fu} = \frac{SiO_2 + Al_2O_3}{Fe_2O_3 + CaO + MgO}$	SOT ^{+))} , FT ^{+))}	Coal	KOVITSKII 1975
$SOT = 929.8 + 4.6 \cdot CaO \cdot MgO - 0.26 \cdot K_2O^2 + 15.7 \cdot P_2O_5 +$ $+ 21.7 \cdot SiO_2 \cdot Na_2O - 7.5 \cdot SO_3 \cdot Na_2O$ $FT = 1448.6 + 3.9 \cdot P_2O_5 \cdot CaO - 0.68 \cdot K_2O^2 + 2.6 \cdot CO_2 \cdot SO_3 -$ $- 12.4 \cdot SO_3 \cdot P_2O_5 + 3 \cdot P_2O_5 \cdot K_2O - 62.7 \cdot P_2O_5 -$ $- 0.29 \cdot SiO_2 \cdot CaO + 2 \cdot SO_3 \cdot K_2O + 1.4 \cdot CO_2 \cdot Cl$	SOT, FT	Biomass	REISINGER 1993
$SOT = 1172 - 53.9 \cdot K + 252.7 \cdot Ca - 788.4 \cdot Mg$ $FT = 1369 - 43.4 \cdot K + 192.7 \cdot Ca - 698 \cdot Mg$	SOT, FT	Biomass	HARTMANN 2000
$SOT = 1.81 \cdot CaO + 4.20 \cdot Al_2O_3 - 2.41 \cdot K_2O + 5.31 \cdot P_2O_5 + 1017$	SOT	Biomass	FRIEDL 2004

^{+))} Results are given in degree Fahrenheit

The applicability of most approaches is to some extent restricted: Most equations have been developed for particular fuels – for coal in many cases – or only melting temperatures under reducing conditions are considered. However, all equations were applied to biomass data and limitations are considered during discussion.

Sum of basic oxides, $R_{b/a}$ and $B/A_{(+P)}$

Since the basic approach is similar for all three indices, the *sum of basic oxides*, $R_{b/a}$ and $B/A_{(+P)}$ are examined together in the following section, and only fuels without additives are taken into account.

Despite considerable variations, a parabolic correlation of the melting temperatures (SOT and FT) as reported in literature [BRYERS 1996, PRONOBIS 2005] can be assumed for all three indices, and also a tendency was found regarding the Si/Al -ratio in the fuel. A more distinct tendency was observed for correlations of characteristic melting temperatures to both $R_{b/a}$ and $B/A_{(+P)}$: In addition to the amount of basic oxides, these indices are also determined by the concentrations of acid oxides, resulting in a more distinct diversification of fuels. High-silica and low-potassium fuels like e.g. Miscanthus are shifted to lower index values, whereas

indices for low-silica fuels like e.g. wood are considerably increased. Calculating $B/A_{(+P)}$, an additional increase is obtained for phosphorous-rich fuels. For all three indices, variations are smaller and correlations are more significant for FT than for SOT.

In Figure 58 softening and flow temperatures are shown vs. the **sum of basic oxides** considering different Si/Al-ratios. Minima for both SOT and FT are assumed at a fraction of basic oxides of 40 % – 50 %. This is in good accordance with BRYERS 1996 where the minimum melting temperatures for coal ashes are reported to be around 75 % and lower values for biomass ashes are stated. HQ wood is found in a narrow range at high fractions of basic oxides of about 75 % – 80 %. LQ wood samples are located at lower values, generally between 55 % and 75 %. Only for two samples i.e. *LQ15* and *LQ17*, even lower values around 40 % were determined. Energy grain and Miscanthus are mainly found at basic oxide fractions below 40 %, and straw is found at minimum temperatures in a range of 40 % – 45 %. However, neglecting particular outliers the variation range of characteristic temperatures at a defined oxide fraction is about 200 °C for FT and 400 °C – 600 °C for SOT.

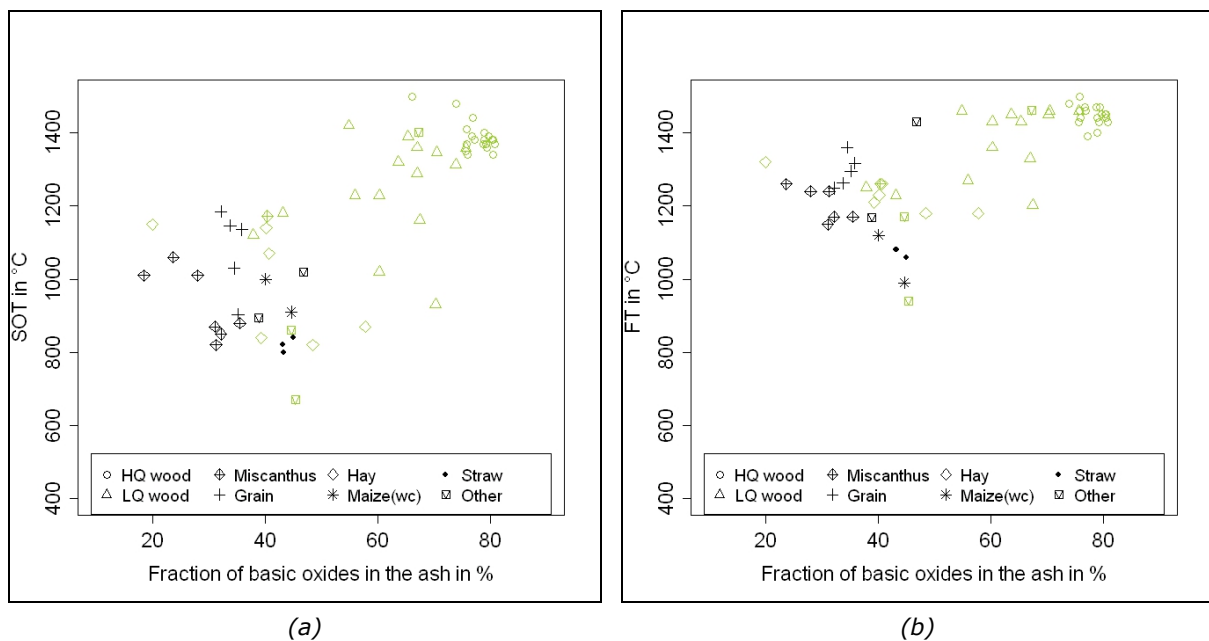


Figure 58: SOT (a) and FT (b) vs. the fraction of basic oxides. Colour of data points is related to Si/Al-ratio. Black: $Si/Al > 30$; Green: $Si/Al < 30$

Also a parabolic tendency for melting temperatures was found for **$R_{b/a}$ -values** in the range of 0-3. $R_{b/a}$ -values > 3 are mainly found for woody biomass, and also for high-Si grain, and no significant correlation to characteristic melting temperatures is determined in this range of values. For high Si/Al-ratios minimum melting temperatures are found around $R_{b/a}=1$, and for lower Si/Al-ratio a minimum around 1.5-1.7 can be assumed.

The additional consideration of phosphorous in the base to acid ratio **$B/A_{(+P)}$** only has a minor effect on the correlation compared to $R_{b/a}$. In Figure 59 SOT and FT vs. $B/A_{(+P)}$ are shown in the range of $B/A_{(+P)}=0-5$ considering different Si/Al-ratios. Compared to $R_{b/a}$, high phosphorous fuels are shifted to higher values. Therefore, the correlations appears more distinct in the range of $B/A_{(+P)}=0-3$, at least for FT. Just as wood, most phosphorous-rich fuels

are located at higher index-values where no correlation to melting temperatures is found any more, and consequently a comparison of the significance of $R_{b/a}$ and $B/A_{(+P)}$ is not possible in this regard.

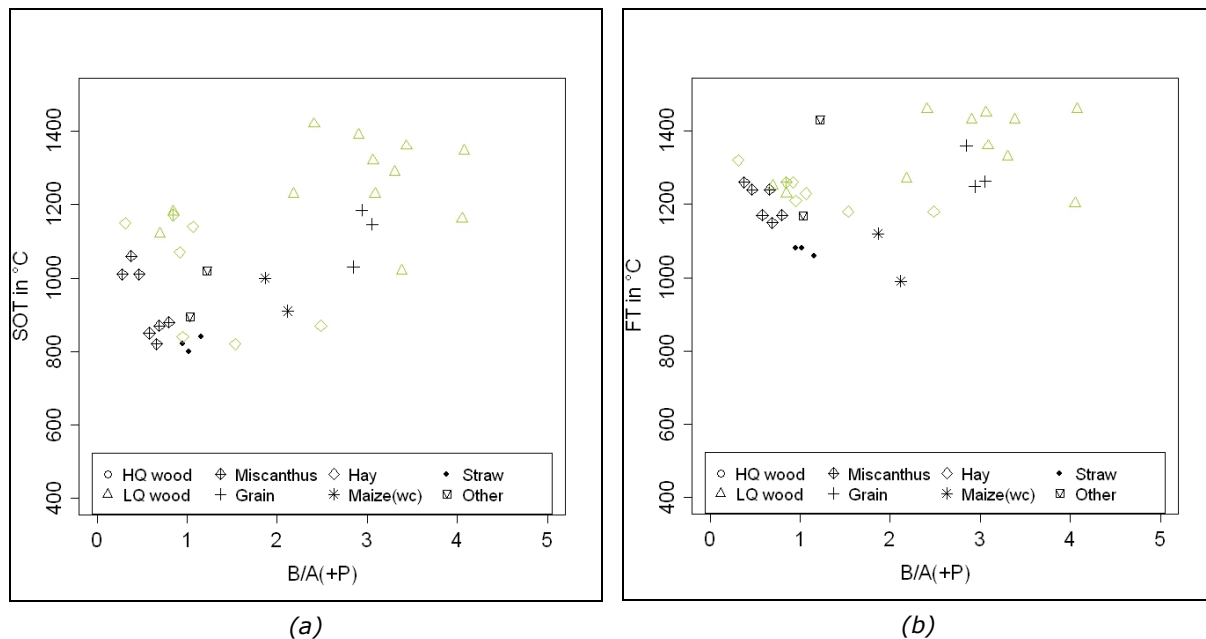


Figure 59: SOT (a) and FT (b) vs. $B/A_{(+P)}$. Colour of data points is related to Si/Al-ratio. Black: Si/Al > 30; Green: Si/Al < 30.

Other elemental ratios

In literature a high **slag viscosity index (S_R)** is related with high viscosity and at the same time low slagging inclination [PRONOBIS 2005, STOIFL 2000]. A tendency of decreasing melting temperatures with increasing S_R -values was found for own biomass data. However, strong variations can be observed which might be explained by the fact that major constituents of biomass ashes like e.g. K_2O or P_2O_5 are not considered in this index. As already found for other indices, variations are smaller and correlations are more significant for FT than for SOT.

The elemental ratio of **Si/(Ca+Mg)** as suggested by LINDSTRÖM 2008 is very similar to the slag viscosity index, and consequently also lower melting temperatures are found with increasing values. However, no correlation and a large variation range of some 100°C for both SOT and FT is found for low values (below 1). This ratio was earlier applied to variations of woody biomass (cf. LINDSTRÖM 2008), however, considering a wide range of raw materials no satisfactory evaluation is obtained.

Another very similar elemental ratio is the correlation **(Si+K+P)/(Ca+Mg)** derived by SOMMERSACHER 2011, dedicated to phosphorous-rich fuels. Similar to the results from the slag viscosity index and the ratio of Si/(Ca+Mg), no significant information was received from that index for the investigated fuels, neither for phosphorous-rich samples: The value received for rape cake e.g. was very close to low quality wood and Miscanthus samples, however the softening temperature is more than 200°C below the values of the sample found in that range.

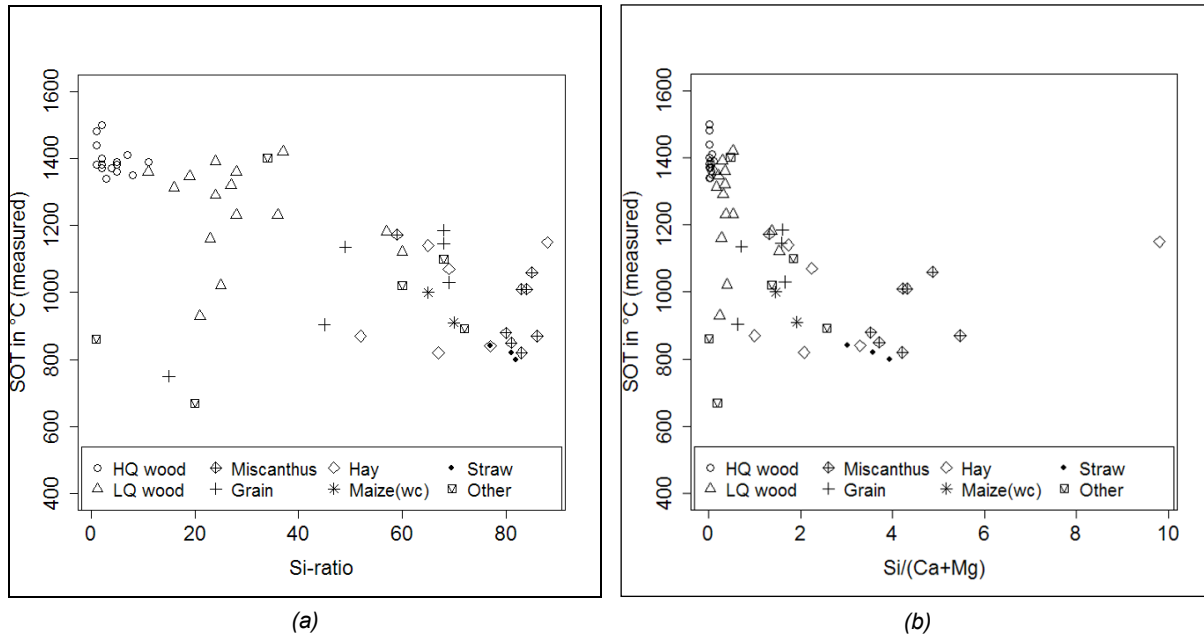


Figure 60: Softening temperature (SOT) vs. slag viscosity index S_R (a) and elemental ratio of $Si/(Ca+Mg)$ (b)

Empirical equations

Equations in BRYERS 1996 are based on the correlation of melting temperatures with sum of basic oxides, and two different approaches are suggested dependent on the ratio of Si/Al (approach 1: $Si/Al \gg 1$ and approach 2: $Si/Al \sim 1$). In Figure 61 calculated values vs. measured values are shown. Approach 1 is applied to Si/Al-ratios lower than 5, and approach 2 for samples with a Si/Al ratio above 30 respectively. To samples with $5 < Si/Al < 30$ both approaches are applied, and results are shown in Figure 61 (a) and (b) for approach 1 and approach 2 respectively. Calculated SOT-values are in good accordance with measured values for Si/Al-ratios lower than 5 and above 30 i.e. mainly HQ wood, Miscanthus and straw. For the major part of samples showing Si/Al-ratios of $5 < Si/Al < 30$ neither of the suggested approaches is well suited. This mainly applies to hay, grain and LQ wood, and thus more than 25 % of the investigated samples are concerned.

No correlation is received using the equation according to **Kovitskii** [KOVITSKII 1975 as cited in BRYERS 1996]. In this equation a linear correlation to an elemental factor is assumed, which is similar to an inverse and simplified base-to-acid ratio. In this regard, two main shortcomings are identified: Potassium and phosphorous are neglected in this equation, although they are major ash constituents in some types of biomass and have considerable effects on ash melting properties. Moreover, according to the equation, low melting temperatures are received for fuels with high Ca- and low Si-concentrations like e.g. woody biomass, and on the other hand highest temperatures will result from Si- and Al-rich fuels like e.g. hay or straw. In Figure 62 calculated values vs. measured values are shown for SOT. All calculated values are found in a small range between 600 °C and 800 °C, and poorest results are received for the fuels with the highest temperatures measured. A similar graph is generated from the calculation of FT-values. Having been developed for coal, this equation

might only be relevant for particular ash compositions that will most probably not be received from biomass combustion.

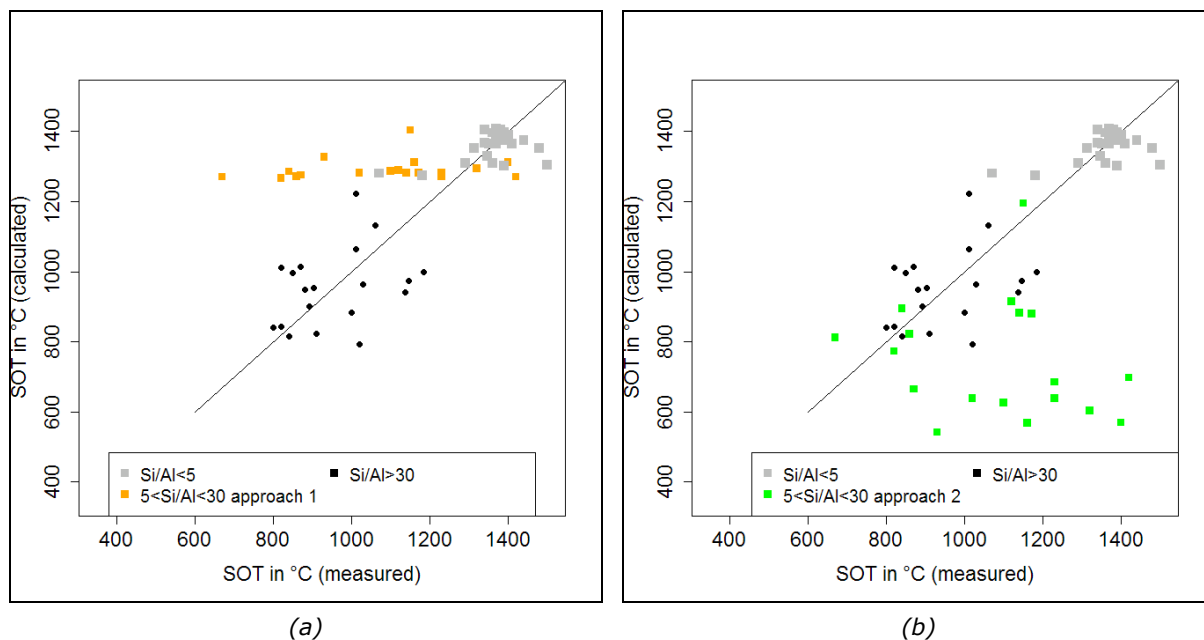


Figure 61: Measured values for SOT vs. predicted values according to the equations of Bryers [BRYERS 1996] (a) using approach 1 (for $Si/Al \gg 1$) for ratios of 5-30 and (b) using approach 2 (for $Si/Al \sim 1$) for ratios of 5-30 for means of comparison.

Applying the equation of **Reisinger** [REISINGER 1993], terms comprising CO_2 -fraction in the fuel ash could not be considered since no carbon-analysis was available for all samples. However, assuming typical values for carbon, sulphur and chlorine, no considerable influence from this reduction can be expected.

In general, calculated SOT-values are too high, and differences to measured values are considerable, showing the strongest deviations for woody biomass. Good correlation to measured values is found for FT-values of straw, Miscanthus and LQ wood. However, no reasonable results are received from this equation for HQ wood, grain and hay samples. Using a large amount of variables, the model seems over-determined for a broad variety of fuels, and provides strong variations for fuel types that were not used for model development.

Temperatures calculated from the equation of **Friedl** [FRIEDL 2004] are in the same range as measured values, but no trend as for measured values is found, showing only small differences among the whole range of fuel samples. This is also true for temperatures resulting when applying the equation of **Hartmann** [HARTMANN 2000]. A possible explanation is that the equation is based on absolute elemental amounts instead of relative values (i.e. concentrations) and thus, only results for fuels with similar ash content can be comparable.

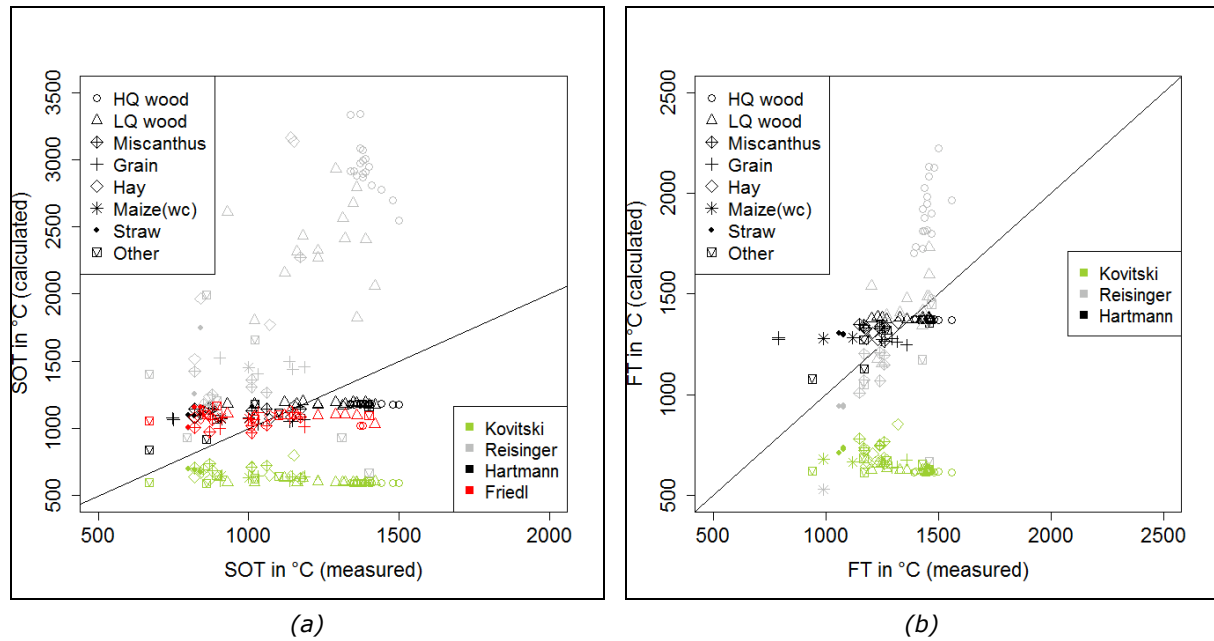


Figure 62: Calculated values vs. measured values for SOT (a) and FT (b) calculated from different empirical equations [KOVITSKII 1975, REISINGER 1993, FRIEDL 2004, HARTMANN 2000].

5.6.2 Practical slagging performance versus theoretical indices

In addition to characteristic melting temperatures, the selected fuel indices (cf. Table 37) were also evaluated regarding their significance for estimating the practical slag formation tendency. Therefore, the quantity of slag formed in combustion tests was evaluated against the selected indices.

Similar tendencies were found for $R_{b/a}$ and $B/A_{(+P)}$. In Figure 63 the respective graphs are shown for wood and wood mixtures (a) and different non-woody biomass fuels (b) from combustion tests as described in section 5.4.2 and 5.4.1 respectively.

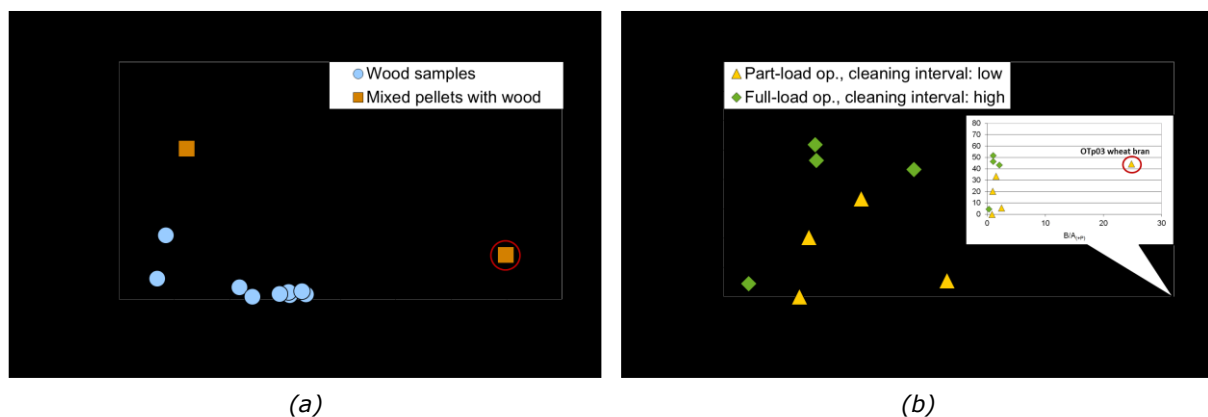


Figure 63: Slag formed during combustion test related to the respective $B/A_{(+P)}$ -value for wood and wood mixtures (a) and different non-woody biomass fuels (b).

For small index values a parabolic trend can be assumed, where the largest slag fractions are found for fuels with $R_{b/a}$ - or $B/A_{(+P)}$ -values of 1.5, and minor slag formation tendency is

observed for fuels with higher or lower index values. However, wheat bran and mixed pellets of wood with maize residues do not follow this trend, showing considerable slag formation despite high index values (slag fraction of 44 % for $B/A_{(+P)}=24.8$ and slag fraction of 15 % for $B/A_{(+P)}=7$ respectively).

Qualitative results from earlier test series show the same tendency. In Figure 64 (a) qualitative assessment of slag formed during combustion tests is presented vs. $B/A_{(+P)}$ -values of the investigated fuels for woody (a) and non-woody (b) biomass (cf. sections 5.4.2.1 and 5.4.3.2). For woody biomass the highest slag formation tendency is observed for fuels with low $B/A_{(+P)}$ -values, and slag formation is still observed for an index value of almost 9. No slag formation is observed for fuels with higher values. However, no further grading is possible: The two fuels with the lowest index value (and almost the same ash content) show considerable differences regarding the extent of slag formation.

$B/A_{(+P)}$ -values of the investigated non-woody biomass fuels are all found in the range of 0 to 4. Except one Miscanthus sample with $B/A_{(+P)}=0.28$ all non-woody biomass fuels formed slag. However, the most severe slagging behavior was observed for index values around 0.5-1. For lower and higher values, a lower slag formation tendency was found.

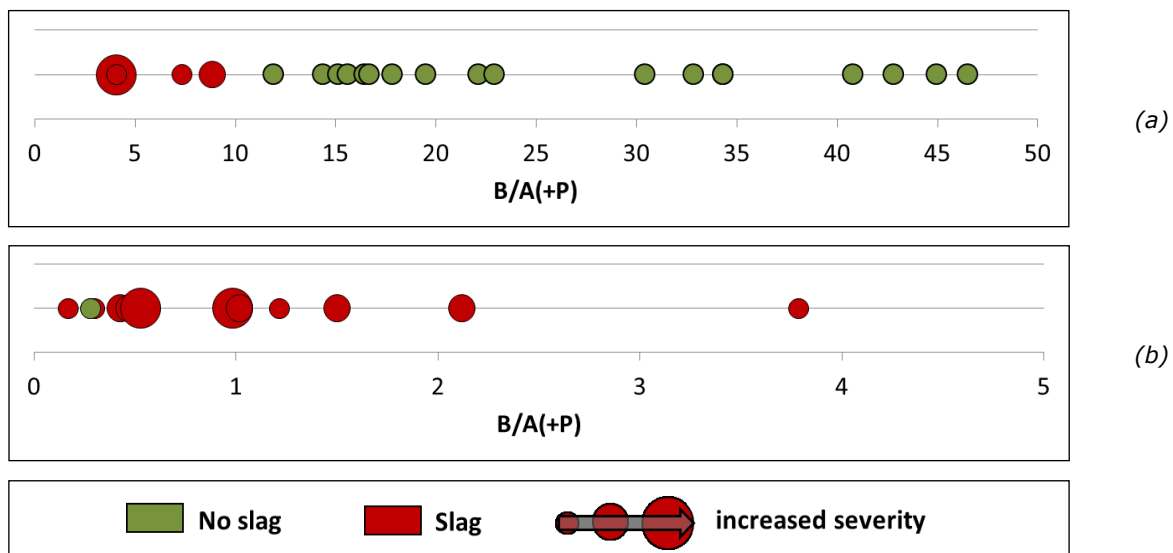


Figure 64: Qualitative assessment of slag formed during combustion tests vs. $B/A_{(+P)}$ -values for woody (a) and non-woody (b) biomass.

No considerable difference was found between $R_{b/a}$ and $B/A_{(+P)}$ regarding the qualitative mapping of the fuels, and phosphorous-rich fuels are shifted to higher values on the x-coordinate. Also a kind of parabolic trend was found for the correlation of slag formation tendency and fraction of **sum of basic oxides**, with maximum slag formation at 40 % – 50 % of basic oxides, which is in good accordance with the respective correlation found for characteristic melting temperatures.

No correlation was found for both silica-ratio and $Si/(Ca+Mg)$. High-silica fuels often tend to form slag, but experiments also showed slagging fuels with low silica ratio on one hand (e.g. wheat bran), and a varying performance was observed for high-silica fuels, from “no slag formation observed” to “severe slag formation”. Therefore, no useful information was

obtained from that indices. In both correlations neither alkaline earth metals nor phosphorous are considered.

5.6.3 Effect of additive utilisation

Additives are usually used with intent to enhance the ash melting behaviour of a particular fuel by changing its elemental composition. The influence of various additives on both ash melting behaviour and slag formation tendency has already been examined (cf. section 5.4.3). In the present chapter the variation of index values by additive admixture is illustrated, and respective changes with regard to ash melting properties are investigated. Based on the findings in previous sections, only indices considering basic and/or acid oxides are taken into account in this regard.

Additives investigated in the present thesis contain Ca, Mg, Si and Al as relevant elements. According to the formulas in Table 37 indices are shifted to higher values by increasing the concentration(s) of Ca and/or Mg, whereas the addition of Al or Si causes a reduction of the respective values.

In Figure 65 characteristic temperatures (SOT (a) und FT (b)) are shown vs. $B/A_{(+P)}$ -values for various straw pellets with and without additives: Pure straw samples are found around $B/A_{(+P)} \approx 1$, representing the lowest melting temperatures. Samples containing additives are distributed over a range from $B/A_{(+P)} = 0.25 - 2.5$. As expected, fuels containing carbonate of lime, lime or DollitTM are represented by indices in the range of 1 – 2.5, and low index-values are found for straw samples with Si- and Al-containing additives (e.g. mullite, AlSiHTM, SialinTM or bauxite). Coming from minimum melting temperatures for pure straw, both additives containing Ca/Mg and additives containing Al/Si show a temperature increasing effect, resulting in a parabolic correlation of melting temperatures vs. $B/A_{(+P)}$ as already found previously (cf. section 5.6.1.).

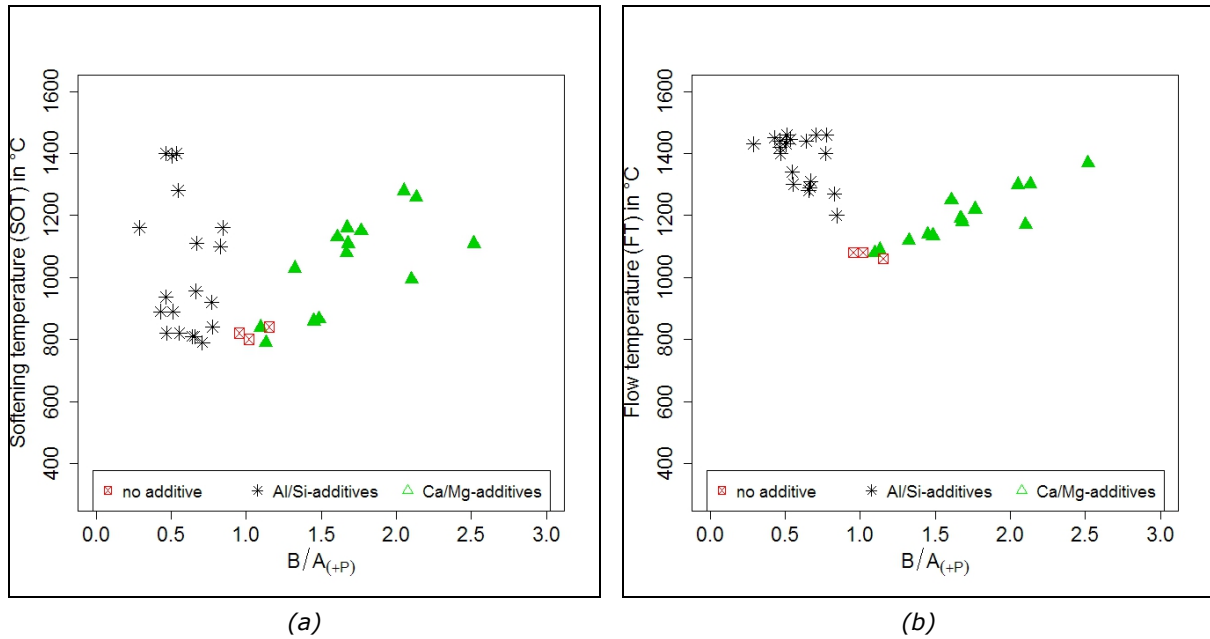
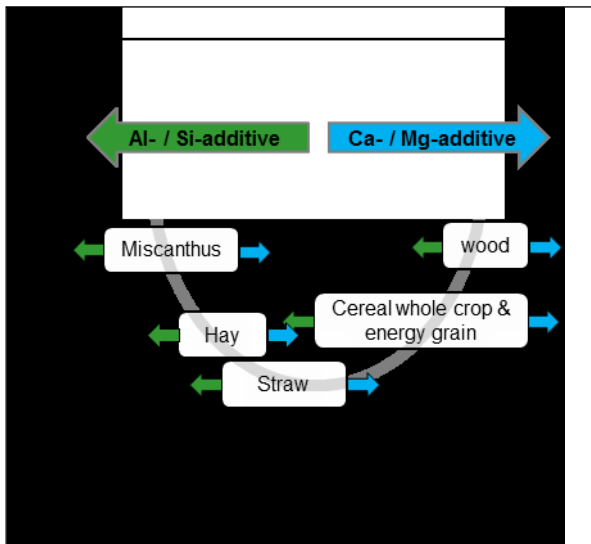


Figure 65: Characteristic temperatures (SOT (a) and FT(b)) vs. $B/A_{(+P)}$ index for straw pellets with and without additives.

It has been shown that particular fuels or raw materials are usually found in a specific range of indices according to their typical elemental composition. Thus, knowing the composition of a particular fuel, the effect of additive admixture can roughly be estimated in advance.

In Figure 67 typical ranges of $B/A_{(+P)}$ -values for various raw materials are shown in a simplified drawing. Moreover, arrows show the direction in which index-values are shifted when particular elements are added (e.g. by using additives or through impurities). $B/A_{(+P)}$ -



values and consequently melting temperatures of wood e.g. are decreasing with increased concentrations of Si or Al, which may be caused by bark-addition or soil contamination. For straw, both Ca/Mg- and Al-containing additives can improve the ash melting properties. However, the melting properties of Miscanthus may even be worsened by adding Ca or Mg.

Figure 66: Simplified drawing of a SOT- $B/A_{(+P)}$ -characteristic showing typical ranges for various raw materials. Arrows show the direction to which index-values are shifted when using particular types of additives.

The drawing in Figure 67 illustrates that additive admixture does not necessarily bring an increase of melting temperatures and thus an improvement of the ash melting properties. Moreover, additives that are useful for one particular raw material can even cause aggravation when applied to another raw material.

5.6.4 Modelling melting temperatures via multivariate calibration

An own calibration model is developed based on obtained fuel data and considering findings from evaluating indices and equations from literature. It is intended to use this model for an estimation of the ash melting properties of new and unknown fuels based on analytical data.

Calculation Procedure

The calculation procedure is briefly described in the following. More detailed information on method and algorithm is available in section 4.8 (Materials and Methods).

Input data: The ash forming elements Al_2O_3 , CaO , Fe_2O_3 , K_2O , MgO , Na_2O , P_2O_5 , SiO_2 were chosen as initial variables for the PLS model. In chapter 5.6.1 a correlation or at least impact of the indices $R_{b/a}$, $B/A_{(+P)}$, *sum of basic oxides* and Si/Al-ratio was shown. From the three similar factors focusing on the basic oxides $B/A_{(+P)}$ was chosen due to its most distinct correlation to melting temperatures and its consideration of phosphorous. Therefore, $B/A_{(+P)}$, the squared $B/A_{(+P)}$ and the Si/Al-ratio have been included. Only data from pure fuels (without additives) were used.

Method, algorithm and optimum complexity of the model: Multivariate calibration was conducted by partial least square regression (PLS) using the SIMPLS-algorithm. The optimum number of PLS components was selected via double cross-validation, searching for a low standard error of prediction (SEP) value using the lowest possible number of components.

Performance criteria: Results were evaluated based on the correlation coefficient between measured and predicted values, and the respective root mean squared error (RMSE) as a measure for prediction errors.

Variable selection: In order to improve the PLS model, variables were reduced aiming at finding the subset of the most relevant variables. Therefore, the following criteria have been applied:

- Variables with a high correlation coefficient to y are preferred
- Variables with a high variance are preferred (variables showing a low variance only provide little information)
- Highly correlated x-variables should be reduced
- The coefficients (E_b) from the full PLS model as a measure of relevance of the particular variables regarding the target value (melting temperature) are considered

Relevance of variables and optimum number of components

The first reduced set of data (R1) was received by removing Al_2O_3 , Fe_2O_3 and Na_2O from the initial set of variables (F) according to their low variance combined with minor correlation to FT/SOT. Moreover, relatively low influence of these variables was found in the PLS-model calculated with the full data set. In addition, $B/A_{(+P)}$ was removed due to its high correlation to $B/A_{(+P)}^2$, keeping the variable showing less correlation to remaining x-variables. A second step of reduction (R2) was done by removing the factors $B/A_{(+P)}^2$ and Si/Al due to the low correlation coefficient to FT/SOT for fuel data. Table 39 gives an overview about parameters used for variable selection, and data sets chosen for calculation are shown.

Table 40: Correlation coefficient for measured and predicted melting temperatures ($cor_{yy'}$), and RMSE for the calculated models (preferred model in bold letters).

Data set	SOT			FT		
	A	R1	R2	A	R1	R2
$cor_{yy'}$	0.79	0.79	0.80	0.72	0.73	0.74
RMSE	137	136	135	98	97	95

A comparison of the performance of the **models for FT und SOT** shows that for SOT the correlation of predicted and measured values is higher, but errors are higher for the resulting predictions when compared to the FT-values. In Figure 67 measured vs. predicted values and predicted values vs. residuals are shown for the SOT- and FT-model calculated based on fuel-data set R2.

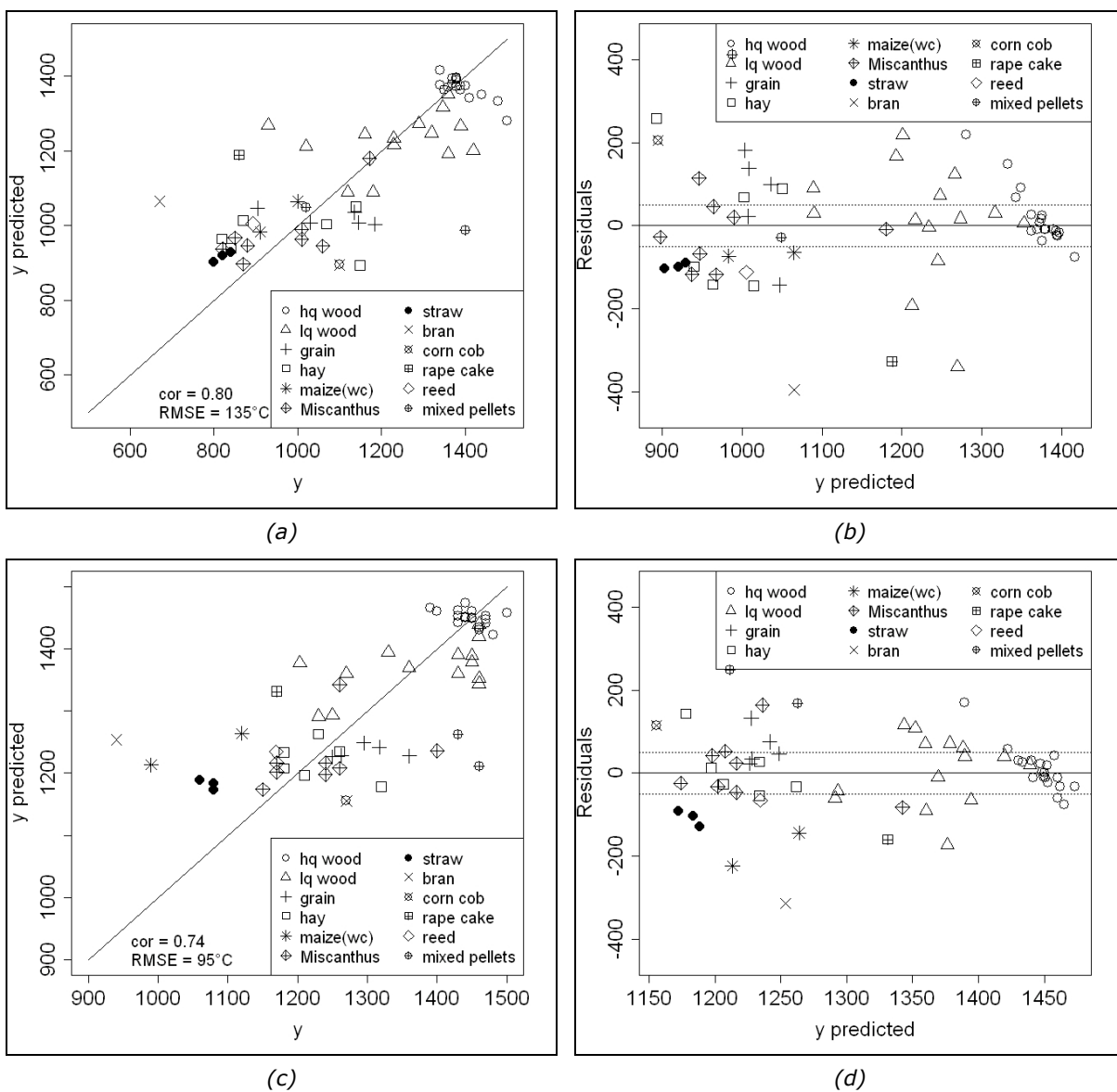


Figure 67: Performance of SOT-model (a)-(b) and FT-model (c)-(d) (fuel-data set R2, 1 PLS component)

41 % and 51 % of the calculated SOT- and FT-values respectively show residuals below 50 °C which is the reproducibility limit according to DIN 51730. Deviations of more than 300 °C are found for predicted FTs and even up to 400 °C for particular SOT-values.

Regarding the fuel classes, major differences between predicted and measured values are observed for maize whole crop, bran and rape cake. However, good prediction is found for Miscanthus and HQ wood, and satisfactory accordance is also found for most LQ wood samples. Positive residuals – i.e. predicted values are lower than measured – are particularly found for mixed pellets, *MI02*, *GR05*, *GR06*, *HQ12*, *LQ11*, *LQ20* and *HAp03*. For maize whole crop, bran, rape cake, and on wood pellets sample (*LQ03*) and all straw samples predicted values are much higher than the measured temperatures.

5.6.5 Discussion

Available indices and equations from literature were investigated and an own calibration model was developed, intending to find a theoretical method to estimate or at least classify ash melting properties of unknown fuels based on common analytical data.

Significance of equations

No practically useful findings are obtained from empirical equations from literature when applied to own biomass data: Calculated melting temperatures often show large deviations – several hundreds °C in some cases – to real values, or only fit particular fuel types.

Simple equations are not applicable to describe complex ash reactions, results from testing available equations show the dilemma: Very sophisticated formulas can provide good accordance of measured and calculated values, resulting in over-determined equations and thus being only applicable to a narrow range of fuels. Equations covering a broad variety of fuel properties on the other hand show considerable variations and consequently do not allow for significant quantitative assessment of particular fuels. An average deviation of 112 °C between calculated and measured SOT-values with maximum deviations of 200 °C–400 °C e.g. are found in REISINGER 1993 when applying his own developed model. Also standard errors of prediction (SEP) of 57 °C for SOT in FRIEDL 2004 and 88 °C and 111 °C for SOT- and FT-prediction respectively in HARTMANN 2000 are found. Confidence intervals of these models therefore clearly exceed the reproducibility limit of 50 °C according to the standard ash fusion test [ÖNORM CEN/TS 15370]. This also applies to the own developed model, where only about 50 % of the calculated values are found to be below this limit.

An aspect of major relevance in this regard is the significance of the ash fusion test: Applicability and reliability of the ash fusion test to the whole range of biomass fuels is frequently doubted [e.g. SKRIFVARS 1999, ÖHMAN 2004 (1)], and thus the development of regression models is affected by an unreliable dependent variable. Moreover, the assessment of practical slagging behavior is problematic due to insufficient significance of characteristic melting temperatures with regard to slag formation tendency in combustion appliances.

Significance of fuel indices

The approach of fuel indices seems more practical, not claiming to provide accurate temperatures but rather classification criteria. However, highly reduced indices considering

only a few ash components are not applicable to the whole range of biomass fuels. Allowing for the large variability all elements that may occur in relevant concentrations need to be considered as discussed in the section *relevant parameters* below.

Among the investigated indices, correlation to characteristic melting temperatures was found for the sum of basic oxides and base-to-acid ratios $R_{b/a}$ and $B/A_{(+P)}$ when applied to own fuel data. A parabolic trend was observed for all three indices, and the most distinct characteristic was found for $B/A_{(+P)}$, still showing a considerable variation range that is possibly also influenced by the deficient reliability of the ash fusion test for particular types of biomass, as already mentioned in the context of equations.

In addition to characteristic melting temperatures, a correlation was also found for practical slag formation tendency in combustion tests and $B/A_{(+P)}$: The degree of slag formation varied dependent on the combustion technology or boiler settings used. However, index values where the maximum slag formation tendency was observed were found to be comparable though.

Due to the considerable variation range, indices can rather be used for an estimation of the melting properties of unknown fuels than to predict concrete melting temperatures. Moreover, indices or characteristic numbers may be used for an assessment regarding the effectivity of additives when applied to particular fuels, or to estimate the properties of ashes from raw material mixtures. Therefore, thresholds have to be specified defining fuel classes with particular melting properties which can then be recommended for particular fields of application. Further development of fuel indices allowing for biomass innate characteristics as well as the broad variety of fuel properties may additionally increase the significance of such indices.

Relevant parameters

The significance of available indices and equations with regard to both characteristic melting temperatures and practical slagging behaviour was investigated, and in addition an own model for calculating melting temperatures was developed. Analysing the results, concentrations of Si, Al, K, P, Ca and Mg are considered as the most relevant parameters when characterising the properties of ashes from solid biomass fuels.

A basic correlation was observed to the sum of basic oxides, i.e. Fe_2O_3 , CaO , MgO , K_2O , Na_2O . However, this number was found to be more distinct and thus significant when related to the acid oxides SiO_2 and Al_2O_3 , and also including P_2O_5 in the basic term. Moreover, characteristic numbers omitting K, P or Al do not show significant correlation to melting properties, as K and P are major constituents of particular types of biomass.

Also, dimensions of the coefficients of the developed regression model are a measure for the influence and consequently the significance of a particular parameter on the result. According to these coefficients, the most significant elemental factor is the ratio of Si to Al, leading to lower melting temperatures with increasing number. Moreover, concentrations of CaO and MgO have an increasing effect in contrast to SiO_2 , K_2O and P_2O_5 .

Hence, these parameters should be included in critical numbers describing the melting or slagging properties of solid biomass ashes. Simplified indices or formulas may also be useful

when applied to restricted and well-defined fuel qualities like e.g. Si-rich/low-Ca fuels or pure woody biomass. This is already done e.g. by BRYERS 1976 providing different formulas dependent on the Si/Al-ratio in the fuel composition, or LINDSTRÖM 2008 using the Si/(Ca+Mg)-ratio as slagging index for woody biofuels.

Shortcomings of available formulas and development potentialities

The investigation of available indices and equations has revealed two main problems, i.e. the scope of application as to the broad variety of biomass fuels, and the interpretation and assessment of the results with regard to practical relevance.

Results show that the applicability of equations or characteristic curve progression is only observed for a defined scope among the whole range of investigated fuels. Moreover, particular fuels show a different characteristic, as observed e.g. for mixed biomass pellets or wheat bran. Therefore, each approach is restricted to a particular scope of application, which needs to be clearly specified. Also the application of different indices for particular fuel types may be useful in order to provide solutions for the whole range of biomass fuels.

A major criterion for the usefulness of a characteristic number is its relevance with regard to practical slagging behavior. Therefore, a particular index value or value range needs to be related to the slag formation tendency in practical combustion appliances. Thus, critical values and fuel classes could be specified and assigned to particular fields of application.

5.7 Theoretic examination of laboratory methods for the determination of ash melting properties

Available methods for the evaluation of the melting properties of biomass ashes are briefly described in section 3.4. These methods have been developed for different purposes and fuels – some of them for coal ashes, some for ashes from solid biomass fuels – and methods considerably differ with regard to evaluation parameter and test procedure.

In the present chapter lab test methods are compared and evaluated regarding their applicability for an assessment of the melting properties of biomass ashes. (Indices and empirical equations are not discussed as they are evaluated in section 5.6.) Therefore, different aspects are examined based on information available from literature: Experimental effort and standardisation potential of the particular test procedures are estimated and test conditions and real combustion conditions are compared. Moreover, nature and quality of the results are discussed, and the significance of these results with regard to real combustion conditions is scrutinised. Since the scope of this chapter is beyond a simple summary of available test methods, it is presented in the "Results and discussion"-section of the thesis instead of the "State of the art and literature review"-part. Moreover, experience and knowledge gained in the context of this thesis form the background for examination and evaluation of the methods.

5.7.1 Aspects on relevance and applicability

General considerations regarding the comparability of test conditions and real combustion conditions, nature and quality of the results, objectiveness as well as experimental effort of a method are presented below. Moreover, lab test methods presented in section 3.4 are surveyed and evaluated in Table 41 and Table 42.

Test conditions versus real combustion conditions

Test conditions of laboratory methods are usually simplified somehow, and consequently the comparability to the real situation is in a way reduced. Therefore, results and conclusions can only be transferred to a limited extent. The main aspects that may be relevant in this regard are summarised below.

Nature of investigated sample

In real combustion appliances, fresh fuel is usually immediately exposed to high temperatures when being fed to the combustion zone, and ash formation, potential ash melting and combustion of fresh fuel take place at the same time. However, most test methods are conducted with laboratory ashes, that are specially produced using defined heating rates and comparably low temperatures and long residence times. Therefore, ash properties may differ when compared to ashes from real combustion processes. Most methods only require small amounts of fuel or ash, and in addition these samples are usually conditioned by milling, sample homogenisation or moulding, thus differing from more inhomogeneous occurrence of fuel and combustion residues forming the fuel bed in typical small-scale combustion units. An

amplified initial shrinkage e.g. was found for the CSIRO test using loose ash compared to investigated methods where previously compacted ash is used [WALL 1998].

Atmosphere

The chemistry of the surrounding atmosphere also has an influence on ash reactions, and in general lower melting temperatures are found for reducing conditions (e.g. BRYANT 2000). Some test methods use gases or gas mixtures in order to create oxidising or reducing conditions, and also air is used in some test procedures. However, also several methods applying inert gas like e.g. nitrogen are found.

Heating rate and residence time

Some test procedures use slow and continuous heating rates, in order to precisely determine the characteristic temperatures. However, applying slow and constant heating rates, long residence times and a defined (e.g. inert) surrounding atmosphere to small and homogenous test samples creates equilibrium like conditions, which are not representative for a typical combustion process. Differences with regard to reaction rates of the melting processes e.g. are not represented by the results of these methods. GUPTA 2007 e.g. stated that fusion temperatures generally significantly decrease if the samples equilibrate at a given temperature for an hour or so.

Mechanical stresses

Particular ash properties like e.g. initial sintering or stickiness are frequently not detected by visual inspection of the sample. Moreover, forces that act on the combustion residues in combustion appliances, exerted e.g. by successive fuel or active ash transport, intensifies the contact of ash/slag particles, thus promoting the formation of agglomerates and lumps.

Nature and quality of results

Precise temperature values or intervals are determined by most methods, describing the melting behaviour of a particular fuel ash. Dependent on the particular method different stages in the melting process (e.g. sintering onset, melting onset,...) are described by these temperatures or temperature ranges. Therefore, samples are either exposed to continuously increasing temperatures like e.g. in the ash fusion test (ÖNORM CEN/TS 15370), or samples are observed at a set of defined temperatures like the compression strength test as described in SKRIFVARS 1998 (cf. chapter 3.4.2). In case of discrete measurement points, the size of the respective interval is decisive with regard to the accuracy of the method. However, methods with a continuous description of the melting process enable a more precise determination of the investigated points.

Some methods result in abstract values comparing a set of samples tested under comparable conditions. No general prediction or quantitative assessment is obtained from indices, which give at most a qualitative idea of the melting and/or slagging tendency.

Apart from the quality of the results, it is important to notice which occurrence or state is determined by the result of the particular method. Most methods e.g. are aiming at the determination of the sintering or melting onset of the ash, other methods describe the point

where a defined amount of ash is already molten. The major issue is to find out the most significant temperature or parameter with regard to practical slag formation tendency.

Experimental effort

Most methods are only tested and applied in one laboratory, where they have been developed. Therefore, only little information is available, and evaluation is done based on descriptions from literature and own assessment using a very simple grading.

Experimental effort of a test method is determined by two major factors, i.e. investment and operating costs for the testing equipment and staff requirements. Test methods that can be conducted with conventional laboratory equipment are differentiated from those that require a particular experimental setup, and in addition a separate category for methods using very expensive test equipment is defined. Regarding staff requirements, three grades are defined, describing methods that can only be conducted by specially skilled personnel, by qualified laboratory staff or that can be applied by any operator.

A further aspect regarding experimental effort is the duration of the test procedure, and three categories are considered to discriminate average test duration from rapid tests and methods that require extensive preparation and/or post-processing or evaluation.

Objectiveness

For some methods, unambiguous procedures are used to determine critical parameters or values, e.g. by analysing threshold values or abrupt changes in a temperature-dependent curve progression. Moreover, detailed descriptions and well-defined categories for sample evaluation are available for several methods that are based on qualitative assessment, thus providing a basis for objective evaluation. On the contrary, several methods may considerably be influenced by the particular operator, requiring interpretation of complex test results (like e.g. curve-progression in thermal analysis) or an assessment of the combustion residues lacking appropriate descriptions (e.g. simple decision if slag was formed or not without defining the characteristics of slag).

As most methods are only tested and used in the laboratory where they have been developed, hardly any information regarding reproducibility is available.

Table 41: Basic information and comparison of test conditions of the investigated methods

Method	Selected references	Evaluation parameter or principle	Tested with / developed for ash from	Test conditions				
				Initial sample (laboratory ash/fuel)	Ash sample (loose ash/moulding)	Heating rate (yes x / no -)	Atmosphere	Mechanical stresses / agitation during heating
Ash Fusion Test (AFT)	DIN 51730, ÖNORM CEN/TS 15370	Shape (optical)	Coal and biomass	Laboratory ash	Moulding	x	Oxidising / reducing	-
Improved Ash Fusion Test ACIRL	WALL 1998	Mechanical stability	Coal	Laboratory ash	Moulding	x	Reducing	x
TMA-Test, CSIRO	GUPTA 1998 (TMA), WALL 1998	Mechanical stability	Coal	Laboratory ash	Loose	x	Inert	x
Melt area fraction (MAF)	KALTSCHMITT 2005	Shape (optical)	Biomass ash	Laboratory ash	Loose	x	inert	-
Compression strength test	SKRIFVARS 1998, AL-OTOOM 2000	Mechanical stability	Coal and biomass	Laboratory ash	Moulding	- [Skrifvars 1998] x [Al-Otoom 2000]	Inert [Al-Otoom 2000] / Air	x (after heating and cooling)
Thermal analysis (TGA, SDTA, STA)	HANSEN 1999, GILBE 2008 (2)	Reaction enthalpy	Biomass	Laboratory ash	Loose	X	Inert / Air	-
Electrical and thermal conductivity	WALL 1998 (HRL, El.), Al-Otoom 2000 (Thermal)	Electrical / thermal conductivity	Coal ash	Laboratory ash	Moulding	x	Reducing	-
Pressure drop technique	AL-OTOOM 2000	Pressure drop	Coal ash	Laboratory ash	Moulding	x	Air	-
Simple oven method (ofi-Method)	ENGLISH 2010	Shape (optical) / mechanical stability	Biomass	Laboratory ash	Moulding	no	Air	x (after heating and cooling)
Rapid test DTI	DAHL 2008	Slag yes/no (optical)	Biomass	Fuel	-	?	Air	-
CIEMAT rapid test	ENGLISH 2010	Amount & hardness of slag	Biomass	Laboratory ash	Loose	x	Air	-
Slag analyzer	HANSEN 2008	Amount & quality of slag	Biomass	Fuel	-	-	Air	-
Standard combustion test + slag characterisation	ÖHMAN 2004 (1), LINDSTRÖM 2007, GILBE 2008 (1)	Amount & quality of slag	Biomass	Fuel	-	Combustion	Air	Dependent on combustion unit

Table 42: Comparison of the method output as well as experimental effort and objectiveness of the investigated methods

Test method	Nature and quality of the results		Experimental effort & objectiveness			
	Indicator(s)	Precision	Equipment o conventional laboratory equipment + special experimental setup ++ expensive instruments required	Staff requirements o any operator + qualified laboratory staff ++ specially skilled personnel	Duration + rapid ++ average +++ long	Objectiveness of evaluation x objectively verifiable - individual interpretation
Ash Fusion Test (AFT)	Temperatures (for characteristic states of melting)	Continuous	++	+	++	X
Improved Ash Fusion Test ACIRL	Temperature of rapid change of ash sample dimension with temperature	Continuous	+	+	++	x
TMA-Test, CSIRO	Temperature of rapid change of ash sample dimension with temperature	Continuous	+	+	++	x
Melt area fraction (MAF)	Temperatures (were 10 % and 50 % of ash are molten)	Continuous	++	+	++	x
Compression strength test	Sintering temperature (=temperature range where pellets start to increase significantly their strength from a baseline value)	Discrete	+	+	++	x
Thermal analysis (TGA, SDTA, STA)	Temperature range (curve describing weight loss and release of heat with increasing temperature)	Continuous	++	++	++	-
Electrical and thermal conductivity	Temperature where the rate of thermal conductivity with temperature increases	Continuous	+	+	++	x
Pressure drop technique	Sintering temperature (the point where the pressure drop reaches a maximum)	Continuous	+	+	++	x
Simple oven method (of-Method)	Qualitative description of ash/slag at defined temperatures	Discrete, qualitative evaluation	o	+	++	-
Rapid test DTI	Qualitative (Slag at defined temp. Yes/no)	Qualitative evaluation	o	o	+	-
CIEMAT rapid test	Qualitative description of ash/slag at defined temperatures	Discrete, qualitative evaluation	o	+	++	-
Slag analyzer	Slagging category (determined based on properties and amount of slag)	Qualitative evaluation	+	+	+++	x
Standard combustion test + slag characterisation	Slagging category (determined based on properties and amount of slag)	Qualitative evaluation	+	+	+++	x

5.7.2 Performance of different methods

Additional information on particular methods apart from simple grading regarding general aspects on relevance and applicability as presented in the previous section is provided below. Strengths and weaknesses are analysed and different methods are compared wherever applicable.

Ash Fusion Test (AFT)

The Ash fusion test is the only standardised procedure among the methods discussed here. However, critical comments are frequently found concerning the ability of characteristic temperatures to describe the melting behaviour of fuel ashes under real combustion conditions and practical slag formation tendency respectively. A comparison of the characteristic temperatures of the AFT with the results from almost all other investigated methods suggests that ash melting already occurs below the lowest characteristic melting temperature: Results from three different methods, i.e. ACIRL, CSIRO and electrical resistance measurements showed that coal ash samples have already reacted at temperatures well below the IDT [WALL 1998]. Moreover, characteristic temperatures indicating considerable slag formation (e.g. T_{50} -temperature) provided by thermomechanical analysis (TMA) are all found clearly below the IDT [BRYANT 2000]. Also, a significant increase of compression strength and thus indication of first sintering or melting reactions was found 400 °C – 500 °C below the softening temperature according to DIN 51730 for both coal ashes [SKRIFVARS 1992] and ashes from various solid biomass fuels [SKRIFVARS 1999]. Results from the melt area fraction (MAF) method showed a melt fraction of about 10 % – 20 % for straw and more than 30 % for a wood sample at IDT [HJULER 2000]. Finally, the melting onset determined via STA (simultaneous thermo analysis) was typically found between 40 °C and 110 °C below the IDT of the standard AFT, showing a qualitative correlation between AFT and STA though [HANSEN 1999].

The reproducibility of IDT is expected to be particularly poor within an interval of slow shrinkage – i.e. a substantial temperature range over which little shrinkage occurs – according to WALL 1998 and GUPTA 1998.

The problem of subjective determination of the characteristic temperatures was eliminated by using clear definitions and computer software for evaluation. However, unexpected changes in shape like e.g. expansion of the sample due to off-gassing might be misinterpreted.

Improved Ash Fusion Test (ACIRL-Test)

Even though first ash reactions were usually determined below the IDT of the standard AFT, good accordance was found between major movement temperature (MMT) and the temperature of 85 % movement with IDT and FT (according to AS1038.15-87) respectively. Compared to the standard ash fusion test, more accurate and objective results can be expected according to KAHRAMAN 1998.

Thermo mechanical analysis (TMA and CSIRO test)

The CSIRO test uses loose ash, resulting in an amplified initial shrinkage compared to procedures using compacted ash (e.g. ACIRL), and therefore provides the most sensitive data

over the complete temperature range according to WALL 1998. Moreover, studies have shown that the melting events observed as coal ash is heated can be reproduced using TMA with much greater accuracy (typically 10 °C in temperature and 5 % in penetration) than the existing AFT test. [WALL 1998]

Melt area fraction (MAF)

Using MAF method delivers more information on the behaviour of the ash during heating, as melting but also sinter and shrinking procedures can be observed. However, highly viscous ash melts or particle agglomeration caused problems in determination. [KALTSCHMITT 2005]

Compression strength test

An additional benefit of this method is that sintering is quantified somehow by the compression strength value. However, overestimations due to discrete measurement have to be considered [AL-OTOOM 2000]. Also, determination problems were shown for high melting ashes: In some cases with woody biomass, the strength again decreased with increasing temperature, most probably due to devolatilisation of some compounds like e.g. CO₂ forming a more porous and unstable ash pellet [LLORENTE 2005]. Moreover, the test was assessed as slow and disadvantageous because of the comparable large samples required [AL-OTOOM 2000].

Thermal analysis (TGA, SDTA, STA)

STA can provide detailed description of ash melting when compared to conventional methods, and the onset of melt formation is determined more precisely. However, additional information and knowledge on components and possible reactions (e.g. from computer-controlled scanning electron microscopy or XRD) is required to enable proper interpretation [Hansen 1999]. Moreover, experts are required to evaluate results from thermal analysis. Results from Bionorm-project stated considerable difficulties in evaluating melting behaviour or even ranking samples [KALTSCHMITT 2005]. In particular the evaluation of Si-rich ashes was considered as problematic [FRANDSEN 2003, GILBE 2008 (2)].

Electrical and thermal conductivity

Only little information about any of those methods is available. Ash reactions were detected at temperatures far below the IDT when using the electrical conductivity method [WALL 1998]. However, no real "breakpoints" could be detected in the curve progression, which is a basic requirement to determine characteristic temperatures.

Regarding thermal conductivity measurements, errors due to the heat flux from the source have to be considered [Al-Otoom 2000].

Pressure drop technique

This method was considered as a fast method, which is sensitive to any changes in the pellet structure. Moreover, different gas conditions and therefore agglomeration in fluidised bed combustion can be simulated. A binder may be required for specific samples, but should not impact the resulting temperature since it disappears at 300 °C. [AL-OTOOM 2000]

Slag analyser

The slag analyser test is conducted with fuel instead of ash samples, and conditions are similar to real combustion appliances. On the other hand, it is not possible to run the test at defined temperatures or – the other way around – specify a characteristic temperature at which melting or slag formation will occur.

According to JENSEN 2012 some issues need special attention and further development of the method respectively: The comparability of fuels with different ash contents is limited as fuels with high ash content are used with a smaller amount in order to avoid choking of the grate at an early stage of the test. Moreover, strong variations of the grate temperature (up to 500 °C – 600 °C) are possible due to bridging, which is occasionally observed – in particular for grain fuels. Even though maximum temperatures of the combustion zone do not vary considerably, it cannot be excluded that this has an impact on amount and properties of the slag formed. Finally, the repeatability of the nature of slag formation may be problematic.

5.7.3 Relevance of test results with regard to practical slagging behavior in small-scale combustion

Only little data is available where slag formation tendency in practical combustion tests is evaluated and compared to results from one of the investigated test methods.

AFT

As the ash fusion test is a standard method since many years, most information is available comparing practical combustion performance to characteristic temperatures of this method. In general, authors state that slag formation could not be appropriately predicted by the results received from the ash fusion test. However, in many cases good qualitative accordance of characteristic temperatures and practical slag formation tendency was found.

Combustion tests with 7 woody biomass fuels in three different combustion technologies are described in ÖHMAN 2004 (1). Therefrom it is concluded that characteristic temperatures determined via AFT (in particular IDT) are not applicable for predicting the slag formation tendency: Even though analysis results indicated that none of the investigated fuels should give any slag in the burners, 6 out of 7 fuels showed at least little slag formation.

Different reed canary grass samples were tested in a 180 kW boiler by PAULRUD 2001, and melting was found to occur at far lower temperatures than determined by the AFT. However, neither qualitative nor quantitative assessment of slag formation is available.

Good qualitative correlation was found by GILBE 2008 (2) when comparing DT and slag formation in a 20 kW underfeed burner, testing 12 different biomass fuels. However, slag formation was poorly predicted, since ash melting already occurred below the predicted temperatures.

MAF

A basic qualitative assessment was applied by HJULER 2002 assigning 12 fuel samples to 2 different classes representing fuels that produced relatively little or no slag that could easily be removed by the ash screw, and fuels that caused significant slag formation and/or fouling, and good accordance was found with results received from MAF method.

TGA

Results from combustion tests in a 50 kW laboratory scale stoker type combustor could be interpreted by investigating the fuel ash via DTA/TGA and additional FT-IR- and XRD-analyses [DARE 2001]. However, inversely predicting the performance based on analyses results seems not possible.

No useful information was received from thermal analysis of the collected slag from 12 different biomass fuels, showing similar results despite considerable differences were found regarding their slag formation tendency. [GILBE 2008 (2)]

5.7.4 Discussion

Different laboratory methods for the determination of ash melting properties were surveyed, and details on test conditions, nature and quality of the test results, experimental effort and objectiveness of the respective methods were compared. Moreover, findings from previous investigations and comparative studies on diverse methods were compiled and analysed, focusing on the methods performance as well as their comparability with findings from real combustion applications.

Performance of test principles and practical relevance of available methods

In many test methods, temperatures or points of particular incidents (e.g. occurrence of a characteristic shape, abrupt change in conductivity or mechanical stability, etc.) are determined for ash samples that are exposed to continuously increasing temperatures.

Findings from previous work show, that critical ash temperatures are usually detected too high, when using the appearance or shape of a sample to indicate changes in the ash structure. Moreover, differences have been observed between loose or compacted ash samples, already giving a certain initial stability to the compacted test specimen. Additionally exerting forces on the sample during test procedure can help to detect earlier stages of sintering or ash melting. Also other properties like e.g. conductivity (thermal or electrical) or compression strength seem to be more suitable to determine initial changes regarding the state of matter of ash. However, the identification of critical temperatures for a quantitative assessment still has to be improved for these methods. Evaluation methods like e.g. qualitative assessment of the stability of agglomerates by manual disintegration seem inadequate for a standard method due to inherent subjectivity. Also a very complex nature of results as received e.g. from thermal analysis showed difficulties regarding a significant and objective interpretation.

As most methods were only used in the laboratories where they have been developed, no information about reproducibility is available for any of them, except the ash fusion test which is applied as standard method since many years. Moreover, none of the methods (except AFT) has been tested for a wide range of biomass fuel qualities.

From the results of most methods, a qualitative grading of different fuel samples is possible – with varying significance. Only little data from real applications is available in order to be compared to laboratory test results, and no adequate estimation or even prediction of the combustion performance in terms of slag formation is provided by any of the investigated

methods. Hence, there is a missing link between the result of a particular method and the performance in practical combustion appliances, implying an adequate method to generally describe the “practical performance”.

General requirements on a suitable test method

The main requirements on a method that predicts slag formation tendency of biomass fuels in small-scale combustion appliances can be summarized as follows:

- Relevance of these results with regard to real combustion performance
- Provision of significant and precise results
- Adequate repeatability and reproducibility (ensured by objectivity of the method)
- Applicability to a wide range of biomass fuels
- Requirement of lowest possible experimental efforts

Aspects on test conditions

Biomass combustion is a complex process. In order to provide a defined and reproducible setting, conditions in test methods need to be simplified, and variance is reduced compared to real combustion conditions. The main differences that may affect the relevance of test results with regard to real application performance have been discussed, namely nature of investigated sample, atmosphere, heating rate, residence time and mechanical stresses.

In spite of a simplified setting, results from test methods can provide valuable information with regard to practical performance. However, parameters or settings that differ from real application should be considered during evaluation of test results, in order to provide for a reasonable and useful interpretation. These factors may also be taken into account for the development of new or optimisation of existing test methods. Moreover, a systematic variation of such parameters could even be part of an evaluation procedure, thus providing additional information.

Nature and quality of test results and respective interpretation

Results of a test method should serve as evaluation criteria, allowing for an assessment of ash melting and slag formation properties of a fuel in combustion appliances. In this regard a particular parameter (e.g. a characteristic temperature) may be used as well as a category or an index derived from several parameters. If the results of a method are discrete values, sufficient intervals are required to ensure an appropriate grading – in particular within a crucial values margin.

For any method, a major challenge is an appropriate interpretation of the test results in terms of specification of the most decisive parameters or resulting factors (e.g. a certain percentage of ash molten, initial melt formation, detection of initial sintering reactions) and respective threshold values to provide adequate information and reliable assessment with regard to practical ash melting and slagging behavior of a biomass fuel. This also requires a suitable method or instrument for a standardised description of the practical slagging performance.

6 Summary and Conclusions

The objective of this work was to investigate ash melting and slag formation on the grate and in the combustion zone of small scale biomass combustion units. Properties and variability of biomass ashes were investigated in this regard, and influencing factors on slag formation were examined considering both fuel related factors and aspects related to the combustion technology. Moreover, methods and approaches for the assessment or classification of melting properties and in particular practical slagging behaviour of biomass ashes were studied.

6.1 Fuel related possibilities to reduce slag formation

Nature and quality of the raw material

Ash composition and consequently ash melting properties are determined by the ash composition, and therefore by the fuel used. Hence, raw material selection is the most decisive issue in this regard. Even though typical characteristics for certain types of raw materials can be specified, considerable variations of elemental composition can be expected among particular raw materials. The most favourable ash melting properties and at the same time least variations can be expected for bark-free stem wood. In contrast, particularly strong variations can be assumed for annual crops and raw material classes comprising a number of different plants and species (like e.g. hay).

Even though elemental composition is mainly determined by plant-innate factors, a certain scope of action to improve the ash melting properties of a biomass fuel is provided by the findings below. However, optimisation in this regard is more easy to realise when using woody biomass compared to non-woody raw materials.

- Bark, wood chips or branches show a higher ash content as well as increased concentrations of particular elements, thus affecting the favourable melting properties of ash from bark-free stem wood.
- Minor influence but still clear variations are attributed to the type of wood. Among the investigated wood species, trouble-free operation can be assumed when using bark-free wood from spruce or pine, whereas somewhat increased slag formation tendency is expected for the combustion of larch.
- The influence of additives in terms of organic binders are estimated to be negligible when used in moderate concentrations (up to 5 %).
- Particular elemental combinations have shown unfavourable ash melting properties (e.g. high-Si/high-K), but elemental composition of a raw material can only be controlled to limited extent. For annual crops improvement may be possible by optimising time of harvest, fertilisation or choice of appropriate plant species. Moreover, contamination with Si-rich soil or sand can promote slag formation by facilitating the formation of low-melting silicates and additionally increasing the ash content of the fuel, and therefore should be avoided.

Potential of raw material blends

Ash melting properties of a fuel are not necessarily improved by admixture of a non-slagging raw material, and resulting blends may even show worse behaviour than each of the pure raw materials. Therefore, the elemental composition needs to be considered when defining the respective raw materials and proportions in a mixture. An improvement of the fuel properties by blending seems possible, but further investigation and experimental validation in this regard is required.

Mineral additives

The admixture of mineral additives can improve ash melting properties and consequently reduce slag formation. Positive effects in this regard were found for Al-, Ca- and Mg-containing additives when applied to straw. However, no ubiquitous application of one particular additive can be recommended for all types of fuels, and additives that are useful for one particular raw material can even cause aggravation when applied to a different raw material. When choosing a particular additive, the elemental composition of the resulting fuel needs to be considered. Moreover, additive fractions should be as small as possible to avoid an undesirable increase of the ash content.

Considering all fuel-related possibilities to reduce slag formation as discussed above, a major prerequisite for all optimisation measures is to know target values, i.e. appropriate fuel properties or significant parameters describing the applicability in this regard need to be specified.

6.2 Requirements for small-scale combustion appliances suited for slagging fuels

General requirements regarding design and settings

Design and settings of combustion technologies considerably influence slag formation in the combustion zone. Short residence time and low temperatures in the grate section may reduce or even prevent ash melting for fuels showing only little slag formation tendency. However, slag formation will not be avoided when firing fuels with specially low melting ashes. Consequently, combustion appliances need to be designed that way that trouble-free operation is possible in spite of slag formation. Therefore, the basic requirement is to enable a consistent transport and discharge of ash and slag through the combustion zone. The most important measures in this regard are:

- Reduce (ash) load of the grate – provide ample dimensioning of the grate section
- Avoid constructive dead zones, bottlenecks and barriers
- Avoid the formation of large slag lumps and agglomerates
- Provide regular agitation of the fuel bed
- Optimise residence time of fuel / combustion residues in the grate section
- Facilitate ash/slag discharge: Provide sufficient space and wide openings for ash/slag discharge, active ash/slag transport and discharge, avoid ash/slag transport through the grate

- Appropriate primary air supply
- Ensure flexibility of boiler settings as to varying fuel properties

Impact of combustion technology on the variability of ash composition

Ash composition is mainly determined by the fuel composition, and variability due to combustion conditions is comparably small. Considerable variations in this regard are only found for Cl, S and Zn, representing only a very small fraction of the whole of ash forming elements. Though these variations may be important regarding the formation particulate emissions, they are of minor relevance for ash melting reactions.

6.3 Relevance of conventional fuel parameters with regard to practical slagging performance

Ash melting properties or slag formation tendency of a particular fuel cannot reliably be predicted based on fuel data in terms of elemental composition, ash content or characteristic melting temperatures from the standard ash fusion test.

Elemental composition

Melting properties of ashes are basically determined by their chemical composition, and Si, Al, K, P, Ca and Mg are identified as the most relevant elements in this regard. However, complex and manifold reactions dependent on initial compounds and surrounding atmosphere as well as additional factors like e.g. reaction rates do not allow for the prediction of precise melting temperatures based on particular elemental concentrations and simple equations. No common method for a reasonable prediction of characteristic melting temperatures or practical slagging performance via empirical equations or regression models has been verified: Either errors of prediction are higher than what seems tolerable in order to provide reliable assessment of a fuel, or models are over-determined, thus being only applicable for a particular type or class of biomass fuels.

Ash content

As melting properties are determined by ash composition, no information about slag formation tendency is gained from knowing the ash content. Regarding only woody biomass fuels, a rough estimation based on the ash content is possible, as increased values in this regard are usually caused by other raw material fractions than bark-free stem wood (e.g. bark or branches) or soil contamination, thus leading to increased slag formation. In general, a significantly increased ash content compared to typical values for a particular fuel may be an indication for contamination or impurities, worsening the slag formation potential. However, no definite assessment is possible in this regard.

Apart from ash chemistry, an increased ash content may promote slag formation for technical reasons though: The ash load on the fuel bed is increased, thus also affecting flow conditions, air supply and consequently temperatures in the grate section. Moreover, contact among ash or slag particles is intensified, thus facilitating the formation of large sintered agglomerates or slag lumps.

Characteristic melting temperatures

It is unanimously agreed among various authors that initial melting is not detected by the characteristic melting temperatures method, which is also confirmed by results from experimental work presented in this thesis: Characteristic melting temperatures from the standard ash fusion test do not appropriately reflect the practical slag formation tendency of a biomass fuel, and consequently no reliable prediction is possible in this regard. Even though a qualitative grading based on characteristic melting temperatures is suitable in many cases, the method is not applicable to the whole range of biomass fuels, and often also quite unrealistic results are received from this test. Moreover, considerable differences are found when applying this method to ash from real combustion tests instead of laboratory ash – in particular for fuels rich in P, K and Si.

Ash melting temperatures are rather over assessed by this method: In general, fuels with low characteristic melting temperatures correspondingly formed slag in real applications, and contrariwise no or little slag formation was received from the combustion of fuels exhibiting high values in this regard. However, in some cases considerable slag formation in spite of high characteristic melting temperatures was found. Moreover, this phenomenon is often observed for problematic fuels where either a grading among slag forming fuels or differentiation of slag forming fuels and non-slagging fuels is required.

On the other hand, fuels showing low melting temperatures may possibly be burnt without major problems – regular ash discharge and agitation of the fuel bed provided – and additional factors like e.g. reaction rate of ash melting or stickiness of the slag formed are assumed to be of major relevance in this regard.

In view of these findings, the specification of a threshold value for any characteristic temperature for means of quality assurance is not reasonable, and alternative methods are required in this regard.

6.4 Classification of biomass fuels with regard to slagging properties

A cluster analysis in the multidimensional space or a classification based on indices both calculated from fuel properties particularly in terms of elemental composition seem to be practicable in order to classify unknown fuels with regard to their slagging properties.

Fuel groups were determined via multivariate data analysis methods based on biomass properties (in terms of ash content and elemental composition), and basically good qualitative agreement was found when comparing the slag formation tendency within and between the respective groups. Thus, e.g. high slagging wood pellets could be identified as they are clearly located outside the cluster of unproblematic high quality wood pellets.

Furthermore, a basic estimation of both ash melting properties and practical slag formation tendency was found for particular fuel indices. In particular the $B/A_{(+P)}$ -index is considered as useful in this regard. A parabolic correlation of slagging performance and $B/A_{(+P)}$ -index can be verified for most fuels, showing severest slag formation for $B/A_{(+P)}$ around 1. However, for high index values – as received e.g. for high-quality wood or P-rich fuels – no differentiation and consequently no grading is possible based on that index. Moreover, sporadically deviations from this correlation are found (e.g. for mixed biomass pellets).

However, further development is required in order to improve the quality of differentiation as well as the significance with regard to slag formation, and thus the applicability for both methods: In both cases, classes with defined slag formation properties need to be specified. In this regard, the problem of finding an adequate measure for an absolute assessment of the practical slag formation tendency still has to be solved. However, an assessment of the applicability of a fuel in terms of slagging performance is only reasonable in the context of defined combustion appliances or technological characteristics.

6.5 Requirements for a lab test method to assess the slag formation tendency of biomass fuels

Currently, there is no reliable method available that provides significant information with regard to practical slag formation tendency of solid biomass, and that is approved to be applicable to a wide range of biomass fuels.

Various demands are made to a method that is suitable for standardisation. Apart from common requirements like objectivity of the method, adequate reproducibility and repeatability, least possible efforts (both personnel and equipment) and short duration, a very important aspect is the relevance of the method with regard to real combustion performance. However, only very little information in this regard is available so far.

Moreover, the following aspects should be taken into account where appropriate:

- Practical tests have shown the relevance of residence time, ash load on the grate, agitation of the fuel bed and prevailing temperature on slag formation. Consequently these aspects shall be considered either by implementation in a method or by estimation of the respective effects when interpreting the test results.
- The method has to be applicable to a broad variety of biomass fuels with different fuel properties.
- The test method shall be applied to the fuel sample rather than laboratory ash of the respective fuel. This is closer to real combustion conditions and also less time-consuming, saving efforts for ash production.

Above all, an appropriate criterion is required to assess the slag formation tendency in real applications. This is essential for being able to evaluate the significance of any method, and to enable clear and unambiguous prediction of the practical performance from a method's results. Linkage of these parameters to technological characteristics of combustion appliances may be useful in this regard.

7 Key findings and future prospects

Benchmarking practical performance

The extent of slag formation in real combustion appliances was used as fundamental assessment criterion. Practical performance was determined in terms of amount or fraction of slag formed during a test run, as well as feasibility or duration of trouble-free operation of a combustion appliance. The main issues of this work, i.e. the significance of indices or particular fuel parameters, the practicability of fuel classification, the influence of technology-related factors were evaluated in this regard.

Further development of the assessment method for practical performance is required in order to provide a more general approach that enables a comparison of results from different combustion technologies. Further research in this regard – which is beyond the scope of this thesis – has been initiated by these results, and already been implemented into an EU-project [AshMelt-Project 2013].

Advanced classification of biomass fuels

Significant information in terms of practical slagging performance was received from both classification using multivariate methods and a fuel index from literature when applied to own data. Based on such property-related classification, groups with specific levels of slagging propensity could be defined, thus allowing for a respective characterisation in a simplified way.

In this regard, further work would be required in order to develop an adequate method and procedure, to ensure reliability and accuracy of the results and to elaborate differentiation within a narrow values range (e.g. among high-quality wood pellets).

A resulting classification method could on one hand be used for an initial assessment of an unknown fuel. On the other hand, requirements for particular fuel classes could be used as target values for means of fuel optimisation or fuel design (e.g. for the determination of appropriate mixing ratios for blended pellets or suitable type and amount of additives).

Factors influencing the slag formation tendency of wood pellets

Impact of type and nature of the raw material on the slag formation tendency of wood pellets was assessed in a qualitative way, and wood species, raw material fraction and organic binders were considered in this regard. The main recommendations for a fuel-related prevention of slag formation are a well-considered utilisation of raw material fractions other than stem-wood, and to avoid contamination of the raw material (e.g. with soil or sand). Moreover, it was shown that wood pellets with relatively low ash content and high characteristic melting temperatures may cause considerable slag formation.

Knowledge gained on wood pellet qualities could be further extended by investigating raw material fractions of other wood species (e.g. different types of hard wood) or woody raw materials of different origin with regard to fuel properties and slag formation tendency. Another issue in this regard is to delimit acceptable proportions of particular raw materials,

not only to keep requirements of quality standards but also to provide for a trouble-free operation.

Fuel design and possibilities to improve fuel properties

A differentiated view on additive utilisation is received from the present work: In accordance with previous findings, a potential positive effect of the admixture of Al-, Ca- or Mg-containing additives was found. However, no generalised solution is advised, as also converse effects may be caused by additive utilisation, and decisions upon type and amount of additive have to be taken individually, dependent to the raw material properties.

Moreover, preliminary investigations of blended pellets showed that ash melting properties and slagging propensity may not simply be forecast based on properties of the pure raw materials.

A main issue with regard to fuel optimisation is to define the target properties of a resulting product, e.g. in terms of elemental composition or other characteristic fuel properties. Therefore, still some basic research is required to gain fundamental understanding of the melting properties and information of practical performance of different types of fuel ashes, and in particular fuel blends.

Systematic examination of technology-related impact

Findings from comparative studies of different combustion technologies using the same biomass fuels and furthermore variation of particular settings allowed for an examination of technology-related aspects on slag formation. Relevant factors in this regard were identified and their impact was described.

Further work in terms of a systematic analysis of these influencing factors (e.g. grate load, residence time, etc.) will enable the assessment or even a quantification of the impact of each parameter on the slag formation and respective combustion performance.

A further step would be the development of specific numbers describing the main characteristics of combustion appliances in this regard in a universal way, thus being applicable to different small-scale appliances and technologies. This would facilitate the specification of technological requirements for a particular fuel and also pave the way for a well-directed development of future combustion technologies in this regard.

State-of-the-art of ash melting tests

Information on available methods was compiled and analysed in a systematic way. Thus, parameters that may influence the quality of the outcome of a test method were identified, and their relevance regarding the significance of the method was estimated.

A comprehensive data set was generated, providing for a comparison of characteristic melting temperatures, elemental composition (index values) and information on practical performance, and the significance of characteristic melting temperatures was found to be inadequate to reliably estimate the slag formation tendency in real combustion units.

Crucial aspects were identified to be considered for further development of ash melting methods by a systematic analysis of the performance of available test methods together with

findings and observations from practical combustion tests (conducted with a broad variation of biomass fuels).

These findings clearly show the need for a new or at least optimised ash melting method, and also provide basic information for initial decisions in this regard (e.g. information on measurement principles, advantages/disadvantages, etc.). Further research in this regard – which is beyond the scope of this thesis – has been initiated by these results, and already been implemented into an EU-project [AshMelt-Project 2013].

8 References

AL-OTOOM 2000

AL-OTOOM, A.Y.; BRYANT, G.W.; ELLIOTT, L.K.; SKRIFVARS, B.J. et.al.: Experimental Options for Determining the Temperature for the Onset of Sintering of Coal Ash. *Energy & Fuels*, Volume 14, pp. 227-233, 2000.

ALAKANGAS 2002

ALAKANGAS, E., PAJU, P.: Wood pellets in Finland – technology, economy, and market, OPET- Report 5, VTT Processes, June 2002.

ARVELAKIS 2001

ARVELAKIS, S.; VOURLIOTIS, P.; KAKARAS, E.; KOUKIOS, E.G.: Effect of leaching on the ash behavior of wheat straw and olive residue during fluidized bed combustion, *Biomass and Bioenergy*, Volume 20, Issue 6, pp. 459–470, June 2001.

ARVELAKIS 2002

ARVELAKIS, S.; KOUKIOS, E.G.: Physicochemical upgrading of agroresidues as feedstocks for energy production via thermochemical conversion methods. *Biomass and Bioenergy*, Volume 22, Issue 5, pp. 331-348, May 2002.

ARVELAKIS 2008

ARVELAKIS, S.; FOLKEDAHN, B.; FRANDSEN, F.J.; HURLEY, J.: Studying the melting behaviour of fly ash from the incineration of MSW using viscosity and heated stage XRD data. *Fuel*, Volume 87 (10-11), pp. 2269-2280, 2008.

ASSENMACHER 2003

ASSENMACHER, W.: *Deskriptive Statistik*. 3. Auflage, ISBN 3-540-00207-3, Springer-Verlag 2003.

BÄFVER 2009

BÄFVER, L.S.; RÖNNBÄCK, M.; LECKNER, B.; CLAESON, F.; TULLIN, C.: Particle emission from combustion of oat grain and its potential reduction by addition of limestone or kaolin. *Fuel Processing Technology*, Volume 90, pp. 353-359, 2009.

BLANDER 1995

BLANDER, M.; RAGLAND, K.W.; COLE, R.L.; LIBERA, J.A.: The inorganic chemistry of wood combustion for power production. *Biomass and Bioenergy* (8), pp. 29-38, 1995.

BOSTRÖM 2009

BOSTRÖM, D.; GRIMM, A.; BOMAN, C.; BJÖRNBOM, E.; ÖHMAN, M.: Influence of Kaolin and Calcite Additives on Ash Transformations in Small-Scale Combustion of Oat. *Energy Fuels*, Volume 23, Issue 10, pp. 5184–5190, October 2009.

BOSTRÖM 2012

BOSTRÖM, D.; SKOGLUND, N.; GRIMM, A.; BOMAN, C.; ÖHMAN, M.; BROSTRÖM, M.; BACKMAN, R.: Ash Transformation Chemistry during Combustion of Biomass, *Energy & Fuels*, Volume 26, Issue 1, pp. 85-93, January 2012.

BRYANT 1998

BRYANT, G.W.; LUCAS, J.A.; GUPTA, S.K.; WALL, T.F.: Use of Thermomechanical Analysis To Quantify the Flux Additions Necessary for Slag Flow in Slagging Gasifiers Fired with Coal. *Energy & Fuels*, Volume 12, pp. 257-261, 1998.

BRYANT 2000

BRYANT, G.W.; BROWNING, G.J.; EMANUEL, H.; GUPTA, S.K.: The Fusibility of Blended Coal Ash. *Energy & Fuels* Volume 14, pp. 316-325, 2000.

BRYERS 1976

BRYERS, R.W.; TAYLOR, T.E.: An examination of the relationship between ash chemistry and ash fusion temperatures in various coal size and gravity fractions using polynomial regression analysis. *Trans. ASME J. Engng Ind.*, 98, pp. 528-539, 1976. (as cited in BRYERS 1996)

BRYERS 1996

BRYERS, RICHARD: Fireside slagging, fouling, and high-temperature corrosion of heat-transfer surface due to impurities in steam-raising fuels. *Progress in Energy and Combustion Science*, Elsevier Science Ltd, 1996.

BUCHEGGER 2011

BUCHEGGER, A.: Development of an Innovative Pellet Burner Concept that Exploits High Ash Fuels and Produces the Lowest Emissions. *Proceedings of the 11th Pellets Industry Forum*, October 4-5, 2011.

- CARVALHO 2007
CARVALHO, L.; WOPIENKA, E.: BeStII – Landwirtschaftliche Brennstoffe für Kleinfeuerungsanlagen. Abschlussbericht zu Arbeitspaket 4: Abbrandversuche. Technical project report, April, 2007.
- CAPABLO 2009
CAPABLO, J.; JENSEN, P.A.; PEDERSEN, K.H.; HJULFER, K.; NIKOLAISEN, L.; BACKMAN, R.; FRANDSEN, F.: Ash Properties of Alternative Biomass. *Energy & Fuels*, Volume 23, Issue 4, pp. 1965-1976, April 2009.
- CLIFTON-BROWN 2002
CLIFTON-BROWN, J.C.; LEWANDOWSKI, I.: Screening *Miscanthus* genotypes in field trials to optimise biomass yield and quality in Southern Germany. *European Journal of Agronomy*, Volume 16, Issue 2, pp. 97-110, March 2002.
- DAHL 2008
DAHL, J.; JUNKER, H.: Characterization of Solid Biofuels 2004 – Development of Methods (PSO project no. 5297), Summary Report and Guidelines. Dong Energy, October 2008.
- DARE 2001
DARE, P.; GIFFORD, J.; HOOPER, R.J.; CLEMENS, A.H.: Combustion performance of biomass residue and purpose grown species. *Biomass and Bioenergy* Volume 21, pp. 277-287, 2001.
- ELLED 2008
ELLED, A.-L.; ÅMAND, L.-E.; ESKILSSON, D.: Fate of Zinc during combustion of Demolition Wood in a Fluidized Bed Boiler. *Energy & Fuels*, Volume 22, Issue 3, pp. 1519-1526, February 2008.
- Englisch 2010
ENGLISCH, M.: DII.2.14 Report on ash melting behaviour. In: BioNormII Pre-normative research on solid biofuels for improved European standards (funded by the European Commission with project number 038644) March, 2010.
- FABER 2012
FABER, M., H.: Statistics and Probability Theory: In Pursuit of Engineering Decision Support. ISBN 978-94-007-4055-6, Springer 2012.
- FRANDSEN 2003
FRANDSEN F.J.: Deposit Formation and Corrosion during Thermal Conversion of Biomass- and Waste -Type Fuels - 2004 State-of-the and Future Challenges. In Frandsen, F.J.: Nordic Ash Course Version 3.0, Graz, December 2003.
- FRANDSEN 2005
FRANDSEN, FLEMING J.; MOIRAGHI, LAURA; VAN LITH, SIMONE; JENSEN, PETER A.: Release of metals, sulphur and chlorine and residual ash formation during biomass combustion on a grate. In: Obernberger, I.; Brunner, T. (Ed.): *Aerosols in Biomass Combustion - Formation, characterisation, behaviour, analysis, emissions, health effects*. Series Thermal Biomass Utilization, Volume 6, pp. 65-77, 2005.
- FRANDSEN 2007
FRANDSEN, F.J.; VAN LITH, S.C.; KORBEE, R.; YRJAS, P.; BACKMAN, R.; OBERNBERGER, I.; BRUNNER, T.; JÖLLER, M.: Quantification of the release of inorganic elements from biofuels. *Fuel Processing Technology*, Volume 88, pp. 1118-1128, 2007.
- FRIEDL 2004
FRIEDL, A.; PADOUVAS, E.; ROTTER, H.; VARMUZA, K.: Prediction of heating value of biomass fuel and ash melting behaviour using elemental compositions of fuel and ash. Poster Presentation: CAC 2004 6, 2004.
- FRIEDL 2006
FRIEDL, G.; FIGL, F.: Pro Pellet I – Schlackebildung und Korrosion in Holzpelletskesseln und Holzpelletsöfen – Arbeitspaket 4: Abbrandversuche. Technical Report, Austrian Bioenergy Centre GmbH, April 2006.
- GILBE 2008 (1)
GILBE, C.; ÖHMAN, M.; LINDSTRÖM, E.; BOSTRÖM, D: Slagging Characteristics during Residential Combustion of Biomass Pellets. *Energy and Fuels*, Volume 22, pp. 3536-3543.
- GILBE 2008 (2)
GILBE, C.; LINDSTRÖM, E.; BACKMAN, R.; SAMUELSSON, R.: Predicting Slagging Tendencies for Biomass Pellets Fired in Residential Appliances: A Comparison of Different Prediction Methods. *Energy & Fuels*, Volume 22, pp. 3680-3686, 2008.

GRIESMAYR 2008

GRIESMAYR, S.; WOPIENKA, E.; HECKMANN, M.; LOHR, M.: Der Europäische Pelletsmarkt (Marktrecherche), Technical report within the project "ProPellet II - Europäische Holzpellets". April 2008.

GUPTA 1998

GUPTA, S.K.; GUPTA, R.P.; BRYANT, G.W.; WALL, T.F. : The effect of potassium on the fusibility of coal ashes with high silica and alumina levels. Fuel Volume 77 (11), pp. 1195-1201, 1998.

GUPTA 2007

GUPTA, R.: Advanced Coal Characterisation: A Review. Energy & Fuels, Volume 21, Issue 2, pp. 451-460, March 2007.

HANEDER 2014

HANEDER, H.; FURTNER, K.: Biomasse – Heizungserhebung 2013. Landwirtschaftskammer Niederösterreich, Abteilung Betriebswirtschaft und Technik (Ed.), May, 2014.

HANSEN 1999

HANSEN, L. A.; FRANDSEN, F. J.; DAM-JOHANSEN, K.; SØRENSEN, SUND, H.: Quantification of fusion in ashes from solid fuel combustion. Thermochemica Acta, Volume 326 (1-2), pp. 105-117, 1999.

HANSEN 2008

HANSEN, H.O.: Measuring solid biofuels' slag tendencies during combustion. 16th European Biomass Conference & Exhibition, 2-6 June 2008, Valencia (Spain), 2008.

HARTMANN 2000

HARTMANN ET AL.: Naturbelassene biogene Festbrennstoffe - umweltrelevante Eigenschaften und Einflussmöglichkeiten. Technischer Bericht, Bayerisches Staatsministerium für Landesentwicklung und Umweltfragen (StMLU) 2000.

HARTMANN 2007

HARTMANN, H.; REISINGER, K.: Feuerungen und Anlagentechnik. In: Hartmann, H. (Hrsg.): Handbuch Bioenergie-Kleinanlagen (2. vollst. überarbeitete Auflage). Sonderpublikation des Bundesministeriums für Verbraucherschutz, Ernährung und Landwirtschaft (BMVEL) und der Fachagentur Nachwachsende Rohstoffe (FNR), Gülzow, 2007.

HARTMANN 2009

HARTMANN, H.; NUSSBAUMER, T.; HOFBAUER, H.; GOOD, J.: Automatisch beschickte Feuerungen. In: Kaltschmitt, M.; Hartmann, H.; Hofbauer, H. (Hrsg.): Energie aus Biomasse – Grundlagen, Techniken und Verfahren. Springer, Heidelberg (2. Auflage), S. 292-533, 2009.

HARTMANN 2013

HARTMANN, H. (HRSG.); REISINGER, K.; TUROWSKI, P.; ROßMANN, P.: Handbuch Bioenergie-Kleinanlagen, Fachagentur Nachwachsende Rohstoffe (FNR) 2013.

HJULER 2000

HJULER, K.: Prediction of fouling and sintering in thermal conversion of biomass – determination of ash fingerprints. 1st World Conference on Biomass for Energy and Industry, 5-9 June 2000, Sevilla (Spain), 2000.

HJULER 2002

HJULER, K.; Use of additives to prevent ash sintering and slag formation. 12th European Conference on Biomass for Energy, Industry and Climate Protection, Amsterdam 17-21 June 2002.

HJULER 2005

HJULER, K.; LARFELD, J.; HOFBAUER, H. ET AL.: Task II.2 – Ash Melting Behaviour. in "Pre-Normative Work on Sampling and Testing of Solid Biofuels for the Development of Quality Assurance Systems, Part 2: Detailed Final Reports. Institute for Energy and Environment GmbH, Leipzig (Germany) 2005.

HOUGH 1990

HOUGH, D.C.; SANYAL, A.; DAVIS, D.G.: ASME Ash Fusion Research Project, American Society Mechanical Engineering Research Committee on Corrosion and Deposits, CRTD-18, New York, 1971. as cited in BRYERS 1996.

HUPPA 1983

HUPPA, M.; BACKMAN, R.: Slagging and fouling during combined burning of bark and oil, gas or peat, in R. W. Bryers (ed.), Fouling of Heat Exchanger Surfaces, pp. 419-432. Engineering Foundation, New York, 1983. As cited in MILES 1996

- JENKINS 1996
JENKINS, B.M.; BAKKER, R.R.; WEI, J.B.: On the properties of washed straw. *Biomass and Bioenergy*, Volume 10, Issue 4, pp. 177-200, 1996.
- JENKINS 1998
JENKINS, B. M.; BAXTER, L.L.; MILES JR., T.R.; MILES, T.R.: Combustion properties of biomass. *Fuel Processing Technology*, Vol. 54 pp. 17-46, 1998.
- JENSEN 2012
JENSEN, T.N.; HANSEN, H.O.; DAHL, J.: Measuring Solid Biofuels' Slag Tendencies during Combustion. Technical Report of Danish Technological Institute, May 2012.
- JÖLLER 2007
JÖLLER, M.: BEST II – Landwirtschaftliche Brennstoffe für Kleinfeuerungsanlagen. Abschlussbericht zu Arbeitspaket 6: Thermodynamische Gleichgewichtsuntersuchungen. Technical Report. April, 2007.
- KAHRAMAN 1998
KAHRAMAN, H.; BOS, F.; REIFENSTEIN, A.; COIN, C.D.A.: Application of a new ash fusion test to Theodore coals. *Fuel* (77), pp. 1005-1011, 1998.
- KALTSCHMITT 2005
KALTSCHMITT, M.; HEIN, M.; MÜLLER-LANGER, F.: Pre-Normative Work on Sampling and Testing of Solid Biofuels for the Development of Quality Assurance Systems. Final Technical Report, Project: Bionorm (Nr. ENK6-CT-2001-00556) funded by the European community under the 5th Framework Programme, April 2005.
- KALTSCHMITT 2009
KALTSCHMITT, M.; HARTMANN, H.; HOFBAUER, H. (HRSG.): *Energie aus Biomasse – Grundlagen, Techniken und Verfahren*. Springer, Heidelberg (2. Auflage), S. 292-533, 2009.
- KNUDSEN 2004
KNUDSEN, J. N.; JENSEN, P. A.; DAM-JOHANSEN, K.: Transformation and Release to the Gas Phase of Cl, K, and S during Combustion of Annual Biomass. *Energy & Fuels*, 18 / 1385-1399, 2004.
- KOVITSKII 1975
KOVITSKII, N.V.: Investigations of the influence of the chemical composition of ash of power coals on its fusibility and viscosity. *Khimiya Tverdogo Topliva* 9 (3): pp. 70-74, 1975. (as cited in BRYERS 1996)
- KRISTÖFEL 2012
KRISTÖFEL, C.; WOPIENKA, E.: Biomass Report. Deliverable 2.3 resulting from work package 2 of the IEE-project MixBioPells (IEE/09/758/SI2.558286), 2012.
- LANG 2006
LANG, T.; JENSEN, P.A.; KNUDSEN, J.N.: The Effects of Ca-Based Sorbents on Sulfur Retention in Bottom Ash from Grate-Fired Annual Biomass. *Energy & Fuels*, Volume 20, pp. 796-806, 2006.
- LEWANDOWSKI 2003
LEWANDOWSKI, I.; CLIFTON-BROWN, J.C.; ANERSSON, B.; BASCH, G.; CHRISTIAN, D.G.; JØRGENSEN, U.; JONES, M.B.; RICKE, A.B.; SCHWARZ, K.U.; TAYEBI, K.; TEIXEIRA, F.: Environment and Harvest Time Affects the Combustion Qualities of Miscanthus Genotypes. *Agronomy Journal* Volume 95, Issue5, pp. 1274-1280, September 2003.
- LINDSTRÖM 2007
LINDSTRÖM, E.; SANDSTRÖM, M.; BOSTRÖM, D.; ÖHMAN, M.: Slagging Characteristics during Combustion of Cereal Grains Rich in Phosphorus. *Energy & Fuels*, Volume 21, pp. 710 – 717, 2007.
- LINDSTRÖM 2008
LINDSTRÖM, E.; ÖHMAN, M.; BACKMAN, R.; BOSTRÖM, D.: Influence of Sand Contamination on Slag Formation during Combustion of Wood Derived Fuels. *Energy & Fuels*, Volume 22, pp. 2216-2220, 2008.
- LIVINGSTON 2006
LIVINGSTON, B.: Biomass ash characteristics and behaviour in combustion systems. IEA Task 32 / Workshop on Ash related Issues in Biomass Combustion, Glasgow, September 2006.
- LLORENTE 2005
LLORENTE, M.J.; GARCÍA, J.E.CARRASCO: Comparing methods for predicting the sintering of biomass ash in combustion. *Fuel* Volume 84, Issues 14-15, pp. 1893-1900, October 2005.
- LLORENTE 2006
LLORENTE, M.J.FERNÁNDEZ.; GARCÍA, J.E.CARRASCO: Concentration of elements in woody and herbaceous biomass as a function of the dry ashing temperature. *Fuel*, 85 / 1273 - 1279, Elsevier, 2006.

LLORENTE 2008

LLORENTE, M.J FERNÁNDEZ.; AROCAS, P.D. ; NEBOT, L.G.; GARCÍA, J.E.CARRASCO: The effect of the addition of chemical materials on the sintering of biomass ash. *Fuel* Volume 87, Issue 12, pp. 2651-2658, September 2008.

MARUTZKY 1999

MARUTZKY, R.; SEEGER, K.: *Energie aus Holz und anderer Biomasse*. DRW-Verlag Weinbrenner GmbH & Co., Leinfelden-Echterdingen, 1999.

MENGEL 1991

MENGEL, K.: *Ernährung und Stoffwechsel der Pflanze*. 7. überarbeitete Auflage, Gustav Fischer Verlag, Jena 1991.

MILES 1996

MILES, T.R.; MILES, JR, T.R.; BAXTER, L.L.; BRYERS, R.W. ET.AL.: Boiler Deposits from firing Biomass Fuels. *Biomass and Bioenergy* (10), pp. 125-138, 1996.

MISRA 1993

MISRA, K.M.; RAGLAND, K.W.; BAKER, A.J.: Wood ash composition as a function of furnace temperature. *Biomass and Bioenergy* (4), pp. 103-116, 1993.

MUSIL-SCHLÄFFER 2010

MUSIL-SCHLÄFFER, B.: *European wood-heating technology survey: An overview of combustion principles and the energy and emissions performance characteristics of commercially available systems in Austria, Germany, Denmark, Norway and Sweden*. Final Report, Nyserda 15566, April, 2010.

NICHOLLS 1940

NICHOLLS, P.; RAIS, W.T.: Viscosity of coal-ash slags. *ASME Transactions*, pp.141-153, 1940. (as cited in REISINGER 1993)

NORDIN 1995

NORDIN, A.: Optimization of sulfur retention in ash when cocombusting high sulfur fuels and biomass fuels in a small pilot scale fluidized bed. *Fuel*, Volume 74, Issu 4, pp. 615-622, 1995.

OBERNBERGER 2001 (1)

OBERNBERGER, I.: Aschen und deren Verwertung. In Kaltschmitt, M.; Hartmann, H. (Hrsg.): *Energie aus Biomasse. Grundlagen, Techniken und Verfahren* (pp. 412-426). Springer Verlag: Berlin-Heidelberg, 2001.

OBERNBERGER 2001 (2)

OBERNBERGER, I.; BRUNNER, T.; JÖLLER, M.: Characterisation and formation of aerosols and fly-ahes from fixed-bed biomass combustion. In Nussbaumer, T. (Ed.): *Aerosols from Biomass Combustion*. International Seminar (International Energy Agency (IEA) BioenergyTask 32: Combustion and Cofiring) at 27 June 2001, Zurich, Switzerland.

OBERNBERGER 2002

OBERNBERGER I., THEK G.: *The current state of Austrian pellet boiler technology; Proceedings of the 1st world conference on Pellets*, Stockholm, Sweden; ISBN 91-631-2833-0, September 2002.

ÖHMAN 1998

ÖHMAN, M.; NORDIN, A.: A new Method for Quantification of Fluidized Bed Agglomeration Tendencies: A Sensitivity Analysis. *Energy & Fuels*, Volume 12, pp. 90-94, 1998.

ÖHMAN 2004 (1)

ÖHMAN M.; BOMAN, C.; HEDMAN, H.; NORDIN, A.; BOSTRÖM, D.: Slagging tendencies of wood pellet ash during combustion in residential pellet burners. *Biomass and Bioenergy*, Volume 27, pp. 585 – 596, 2004.

ÖHMAN 2004 (2)

ÖHMAN, M.; BOSTRÖM, D.; NORDIN, A.; HEDMAN, H.: Effect of Kaolin and Limestone Addition on Slag Formation during Combustion of Wood Fuels. *Energy & Fuels* 18, pp. 1370-1376, 2004.

ÖHMAN 2004 (3)

ÖHMAN, M.; NORDIN, A.; HEDMAN, H.; JIRJIS, R.: Reasons for slagging during stemwood pellet combustion and some measures for prevention. *Biomass and Bioenergy*, Volume 27, Issue 6, pp. 597-605, December 2004.

OLANDERS 1995

OLANDERS, B.; STEENARI, B.-M.: Characterization of ashes from wood and straw. *Biomass and Bioenergy* Volume 8, Issue 2, pp. 105-115, 1995.

- PAULRUD 2001
PAULRUD, S.; NILSSON, C.; ÖHMAN, M.: Reed canary-grass ash composition and its melting behaviour during combustion. *Fuel* 80, pp. 1391-1398, 2001.
- PRONOBIS 2005
PRONOBIS, M.: Evaluation of the influence of biomass co-combustion on boiler furnace slagging by means of fusibility correlations. *Biomass and Bioenergy* 28, pp. 375-383, 2005.
- RADEMACHER 2005
RADEMACHER P.: Nährelementgehalte in den Kompartimenten wichtiger Wirtschaftsbaumarten und deren Bedeutung für die Reststoffverwertung. *Holz als Roh- und Werkstoff* (2005) 63: pp. 285-296. Springer-Verlag 2005.
- REISINGER 1993
REISINGER, K.: Bestimmung des Ascheschmelzverhaltens verschiedener Biomassearten und Auswertung der Ergebnisse im Hinblick auf eine sinnvolle thermische Nutzung. Diplomarbeit, Institut für Verfahrenstechnik, Brennstofftechnik und Umwelttechnik der Technischen Universität Wien, 1993.
- SCHMITT 2013
SCHMITT, V.E.M.; KALTSCHMITT, M.: Effect of straw proportion and Ca- and Al-containing additives on ash composition and sintering of wood-straw pellets. *Fuel* Volume 109, pp. 551-558, July 2013.
- SCHWABL 2013
SCHWABL, M.; HASLINGER, W.: AshMelTproject - Publishable Summary for the Reporting period 01.Jan. 2012 – 31. Mar. 2013. Downloaded from www.ashmelt.eu, January 20, 2014.
- SEGGIANI 1999
SEGGIANI, M.: Empirical correlations of the ash fusion temperatures and temperature of critical viscosity for coal and biomass ashes. *Fuel* Volume 78 (9), pp. 1121-1125, 1999.
- SKRIFVARS 1992
SKRIFVARS, B.-J.; HUPPA, M.: Sintering of Ash during Fluidized Bed Combustion. *Ind.Eng.Cem.Res.* Volume 31, pp. 1026-1030, 1992.
- SKRIFVARS 1998
SKRIFVARS, B.-J.; BACKMAN, R.; HUPA, M.: Characterization of the sintering tendency of ten biomass ashes in FBC conditions by a laboratory test and by phase equilibrium calculations. *Fuel Processing Technology* (56), pp. 55-67, 1998.
- SKRIFVARS 1999
SKRIFVARS, B.-J.; ÖHMAN, M.; NORDIN, A.; HUPA, M.: Predicting Bed Agglomeration Tendencies for Biomass Fuels Fired in FBC Boilers: A Comparison of Three Different Prediction Methods. *Energy & Fuels* 13, pp. 359-363, 1999.
- SOMMERSACHER 2011
SOMMERSACHER, P.; BRUNNER, T.; OBERNBERGER, I.: Fuel Indexes: A Novel Method for the Evaluation of Relevant Combustion Properties of New Biomass Fuels. *Energy & Fuels* Volume 26 (1), pp. 380-390, January 2012.
- STEENARI 1998
STEENARI, B.-M.; LINDQVIST, O.: High-temperature reactions of straw ash and the anti-sintering additives kaolin and dolomite. *Biomass and Bioenergy*, 14 (1) pp. 67-76, 1998.
- STEENARI 2009
STEENARI, B.-M.; LUNDBERG, A.; PETTERSSON, H.; WILEWSKA-BIEN, M.; ANDERSSON, D.: Investigation of Ash Sintering during Combustion of Agricultural Residues and the Effect of Additives. *Energy & Fuels*, Volume 23, Issue 11, pp.5655-5662, November 2009.
- STOIFL 2000
STOIFL, B.: Energetische Nutzung von Stroh in kalorischen Kraftwerken anhand eines konkreten Beispiels – Wärmekraftwerk Dürnrohr. Diplomarbeit, Technische Universität Wien, 2000.
- TANGSATHITKULCHAI 2001
TANGSATHITKULCHAI, C.; TANGSATHITKULCHAI, M.: Effect of bed materials and additives on the sintering of coal ashes relevant to agglomeration in fluidized bed combustion. *Fuel Processing Technology*, Volume 72, pp. 163-183, 2001.
- THY 2000
THY, P.; LESHER, C.E.; JENKINS, B.M.: Experimental determination of high-temperature elemental losses from biomass slag. *Fuel*, Volume 79, pp. 693-700. 2000.

- THY 2006 (1)
 THY, P.; JENKINS, B.M.; GRUNDTVIG, S.; SHIRAKI, R.; LESHER, C.E.: High temperature elemental losses and mineralogical changes in common biomass ashes. *Fuel*, Volume 85, pp. 783-795, 2006.
- THY 2006 (2)
 THY, P.; JENKINS, B.M.; LESHER, C.E.; GRUNDTVIG, S.: Compositional constraints on slag formation and potassium volatilization from rice straw blended wood fuel. *Fuel Processing Technology*, Volume 87, pp.383-408, 2006.
- TURN 1997
 TURN, S.Q.; KINOSHITA, C.M.; DARREN, M.I.: Removal of inorganic constituents of biomass feedstocks by mechanical dewatering and leaching. *Biomass and Bioenergy*, Volume 12, Issue 4, pp. 241-252, 1997.
- VAN LITH 2006
 VAN LITH, S.C.; ALONSO-RAMIREZ, V.; FRANDSEN, F.J.; GLARBORG, P.: Release to the Gas Phase of Inorganic Elements during Wood Combustion. Part 1: Development and Evaluation of Quantification Methods. *Energy and Fuels*, 20, pp. 964-978, 2006.
- VAN LITH 2008
 VAN LITH, S.C.; JENSEN, P.A.; FRANDSEN, F.J.; GLARBORG, P.: Release to the Gas Phase of Inorganic Elements during Wood Combustion. Part 2: Influence of Fuel Composition. *Energy & Fuels*, Folume 22, pp. 1598-1609, 2008.
- VARGAS 2001
 VARGAS, S.; FRANDSEN, F.J.; DAM-JOHANSEN, K.: Rheological properties of high-temperature melts of coal ashes and other silicates. *Progress in Energy and Combustion Science*, Volume 27 (3), pp. 237-429, 2001.
- VARMUZA 2009
 VARMUZA, K.; FILZMOSER, P.: *Introduction to Multivariate Statistical Analysis in Chemometrics*. ISBN: 9781420059472, CRC Press, 2009.
- VASSILEV 1995
 VASILEV, S.V.; KITANO, K.; TAKEDA, S.; TSURUE, T.: Influence of mineral and chemical composition of coal ashes on their fusibility. *Fuel Processing Technology*, Volume 42, Issue 1, pp. 27-51, March 1995.
- VASSILEV 2013
 VASSILEV, S.V.; BAXTER, D.; ANDERSEN L.K.; VASSILEVA C.G.: An overview of the composition and application of biomass ash. Part 2. Potential utilisation, technological and ecological advantages and challenges. *Fuel*, Volume 105, pp. 19-39, March 2013.
- VASSILEV 2014
 VASSILEV, S.V.; BAXTER, D.; VASSILEVA, C.G.: An overview of the behaviour of biomass during combustion: Part II. Ash fusion and ash formation mechanisms of biomass types. *Fuel*, Volume 117, Issue PART A, Pages 152-183, January 2014.
- WALL 1998
 WALL, T.F.; CREELMAN, R.A.; GUPTA, R.P.; GUPTA, S.K.: Coal ash fusion temperatures-New characterization techniques, and implications for slagging and fouling. *Progress in Energy and Combustion Science*, Volume 24, pp. 345-353, 1998.
- WANG 2014
 WANG, L.; SKJEVRAK, G.; HUSTAD, J.E.; SKREIBERG, Ø.: Investigation of Biomass Ash Sintering Characteristics and the Effect of Additives. *Energy & Fuels*, Volume 28, Issue1, pp. 208-218, January 2014.
- WOPIENKA 2007
 WOPIENKA, E.; CARVALHO, L.; FRIEDL, G.: Combustion Behaviour of various Agricultural Biofuels – Emissions and Relevant Combustion Parameters. *Bioenergy 2007 – International Bioenergy Conference and Exhibition*, September 3-6, Jyväskylä (Finland) 2007.
- WOPIENKA 2008
 WOPIENKA, E.; EMHOFER, W.; JÖLLER, M.; EVIC, N.: Verbrennungsversuche und thermodynamische Gleichgewichtsberechnungen, Technical report within the project "ProPellet II - Europäische Holzpellets". October 2008.
- WOPIENKA 2012
 WOPIENKA, E.; KRISTÖFEL, C.; KALLIO, M.; ZENG, T.: Production and combustion tests of alternative and mixed biomass pellets. Technical Report, IEE/09/758/SI2.558286 – MixBioPells (WP 3 / O 3.3), 2012.

- WOJCIK 2013
WOJCIK, M.; ENGLISH, M.: Memorandum of the ISO TC 238 Meeting in Bangkok (18th -23rd of March 2013) for the national standardization committee ON-K241, April 2013.
- WU 2011
WU, H.; CASTRO, M.; JENSEN, P.A.; FRANDSEN, F.J.; GLARBORT, P.; DAM-JOHANSEN, K.; RØKKE, M.; LUNDTORP, K.: Release and Transformation of Inorganic Elements in Combustion of a High-Phosphorus Fuel. *Energy & Fuels*, Volume 25, pp. 2874-2886, May 2011.
- XIONG 2008
XIONG, S.; BURVALL, J.; ÖRBERG, H.; KALEN, G.; THYREL, M.; ÖHMAN, M.; BOSTRÖM, D.: Slagging Characteristics during Combustion of Corn Stovers with and without Kaolin and Calcite. *Energy & Fuels*, Volume 22, Issue 5, pp. 3465-3470, September 2008.
- YIN 2008
YIN, C.; ROSENDAHL, L.A.; KÆR, S.K.: Grate-firing of biomass for heat and power production. *Progress in Energy and Combustion Science*, Volume 34 (6), pp. 725-754, 2008.
- ZEVENHOVEN-ONDERWATER 2001
ZEVENHOVEN-ONDERWATER, M.; BACKMAN, R.; SKRIFVARS, B.-J.; HUPA, M.: The ash chemistry in fluidised bed gasification of biomass fuels. Part I: Predicting the chemistry of melting ashes and ash-bed material interaction. *Fuel* (80), pp. 1489-1502, 2001.

Standards and quality labels

- ASTM D1857M
ASTM D1857M: Standard Test Method for Fusibility of Coal and Coke Ash. April, 2010.
- DIN 51719
DIN 51719: Testing of solid fuels - Solid mineral fuels - Determination of ash content. German Institute for Standardization (Ed.), July 1997.
- DIN 51730
DIN 51730:2007-9: Prüfung fester Brennstoffe – Bestimmung des Asche-Schmelzverhaltens, German Institute for Standardization (Ed.), September 2007.
- DIN 51731
DIN 51731_1996-10: Testing of solid fuels - Compressed untreated wood - Requirements and testing, (document already recalled)
- DINplus 2004
DINplus Zertifizierungsprogramm: Holzpellets zur Verwendung in Kleinf Feuerungsstätten nach DIN 51731 – HP 5 (ÖNORM M 7135 – HP1). DIN CERTCO DIN CERTCO Gesellschaft für Konformitätsbewertung mbH (Ed.), Januar 2004.
- Directive 2009/28/EC
Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC, <http://eur-lex.europa.eu> on June 11th 2014
- ÖNORM CEN/TS 14918
ÖNORM CEN/TS 14918: Solid biofuels — Determination of calorific value. Austrian Standards Institute (Ed.), September 2006.
- ÖNORM CEN/TS 15370-1
ÖNORM CEN/TS 15370-1:2006 12 01: Solid biofuels – Method for the determination of ash melting behaviour, Part 1: Characteristic temperatures method. Austrian Standards Institute (Ed.), Wien 2006.
- ÖNORM CEN/TS 14774-2
ÖNORM CEN/TS 14774: Solid biofuels - Methods for the determination of moisture content - Oven dry method - Part 2: Total moisture - Simplified method. Austrian Standards Institute (Ed.), November, 2004.
- ÖNORM CEN/TS 14775
ÖNORM CEN/TS 14775: Solid biofuels - Method for the determination of ash content. Austrian Standards Institute (Ed.), November 2004.

- ÖNORM EN 14961-1
ÖNORM EN 14961-1:2010 04 01: Feste Biobrennstoffe - Brennstoffspezifikationen und -klassen - Teil 1: Allgemeine Anforderungen, April 2010.
- ÖNORM EN 14961-2
ÖNORM EN 14961-2:2011 07 15: Feste Biobrennstoffe - Brennstoffspezifikationen und -klassen - Teil 2: Holzpellets für nichtindustrielle Verwendung. Austrian Standards Institute (Ed.), July 2011.
- ÖNORM EN 14775
ÖNORM EN 14775: Solid biofuels – Determination of the ash content. Austrian Standards Institute (Ed.), November 2012.
- ÖNORM CEN/TS 15104
ÖNORM CEN/TS 15104: Solid biofuels - Determination of total content of carbon, hydrogen and nitrogen - Instrumental methods. Austrian Standards Institute (Ed.), October 2005.
- ÖNORM CEN/TS 15148
ÖNORM CEN/TS 15148: Solid biofuels - Method for the determination of the content of volatile matter. Austrian Standards Institute (Ed.), February 2006.
- ÖNORM CEN/TS 15289
ÖNORM CEN/TS 15289: Solid Biofuels - Determination of total content of sulphur and chlorine. Austrian Standards Institute (Ed.), June 2006.
- ÖNORM CEN/TS 15290
ÖNORM CEN/TS 15290: Solid Biofuels - Determination of major elements. Austrian Standards Institute (Ed.), May 2006.
- ÖNORM CEN/TS 15297
ÖNORM CEN/TS 15297: Solid Biofuels - Determination of minor elements. Austrian Standards Institute (Ed.), May 2006.
- ÖNORM M 7135
ÖNORM M 7135:2000 11 01: Presslinge aus naturbelassenem Holz oder naturbelassener Rinde - Pellets und Briquets - Anforderungen und Prüfbestimmungen, Austrian Standards Institute (Ed.), November 2000. (Document already recalled on February 15 2013)

Websites

- AshMelt-Project 2013
<http://www.ashmelt.eu/> on december 30th, 2013
- ETA 2013
PelletsCompact ETA PC 20, 25 und 32 kW (product information) retrieved from <http://www.eta.co.at/254.0.html> on december 30th, 2013
- KWB 2013
Product information on KWB powerfire, retrieved from <http://www.kwb.at/de/produkte/kwb-powerfire-hackgut-pellets/vorteile-innovationen.html> on december 30th, 2013
- R-project 2008
R: Software, a language and environment for statistical computing. R Development Core Team, Foundation for Statistical Computing, www.r-project.org, Vienna, Austria, 2008.
- R-packages
List of contributed packages retrieved from <http://cran.r-project.org/web/packages/> on September 18th, 2011

9 Annex I – Abbreviations and List of symbols

ADP, ATP	Adenosine diphosphate, Adenosine triphosphate
AFT	Ash Fusion Test
B/A _(+P)	Base/Acid-ratio (including phosphorous)
BA	Bottom Ash
CFBA	Controlled fluidised bed agglomeration
dp _{CH}	Pressure difference in the chimney
DSC	Differential scanning calorimetry
DT	Deformation Temperature (ref. to ÖNORM CEN/TS 15370)
E _b	Coefficients in regression model
FT	Flow Temperature (ref. to ÖNORM CEN/TS 15370 and DIN 51730)
GR	Fuel ID for grain
HA	Fuel ID for hay
HE	Heat exchanger
HHV	Higher heating value
HQ	Fuel ID for high quality wood
HT	Hemispheric/Hemisphere Temperature (ref. to ÖNORM CEN/TS 15370 and DIN 51730)
IC	Ion chromatography
IDT	Initial Deformation Temperature (ref. to ASTM D1857M)
IQR	Interquartile range
LHV	Lower heating value
LQ	Fuel ID for low quality wood
MAD	Median average deviation
MAF	Melt area fraction
MC	Fuel ID for maize whole crop
MI	Fuel ID for Miscanthus
Mx	Fuel ID for blended pellets
NDIR	Non-dispersive infrared sensor
OT	Fuel ID for other biomass (not one of the defined fuels)
PC1, PC2,...	Principal Component number 1, 2, ...
PCA	Principal Component Analysis
PLS(R)	Partial least square regression
Q ₁ , Q ₂ ,...	First Quartil, Second Quartil, ...
QD	Quartile deviation
R _{b/a}	Base/Acid-ratio

RSME	Root mean squared error
SDTA	Simultaneous differential thermal analysis
SEP	Standard error of prediction
SL	Slag
SOT	Softening Temperature (ref. to DIN 51730)
SPT	Spherical Temperature (ref. to DIN 51730)
S _R	Silica-ratio
SST	Shrinkage Starting Temperature (ref. to ÖNORM CEN/TS 15370)
ST	Fuel ID for straw
STA	Simultaneous thermal analysis
T _{CC}	Temperature (combustion chamber)
T _{FB}	Temperature (fuel bed)
T _{feed}	Temperature (feed)
T _{FG}	Temperature (flue gas)
TGA	Thermal gravimetric analysis
TMA	Thermo-mechanical assessment
T _{return flow}	Temperature (return flow)
\dot{V}_{Feed}	Volume flow feed
wt%	Percentage by mass

10 Annex II – List of tables

Table 1: Non-woody biomass identified as potential raw materials for fuel production in different European countries (i.e. Austria, Denmark, Finland, Germany, Italy, Spain and Sweden) classified according to the origin of the raw material. [KRISTÖFEL 2012].	6
Table 2: Specification of wood pellet qualities according to ÖNORM EN 14961-2 and previous national standards and quality labels for selected countries [GRIESMAYR 2008].	8
Table 3: Function and occurrence of relevant plant nutrients [MENDEL 1991].	13
Table 4: General processes of physico-chemical transformations observed in biomass ashes by VASSILEV 2014.	15
Table 5: Primary products of ash-forming elements from the initial stages of combustion (divided into basic and acidic compounds and arranged according to reactivity) according to BOSTRÖM 2012.	17
Table 6: Typical compounds in ash and slag samples from the combustion of different biomass fuels, summarised from OLANDERS 1995, GILBE 2008 (1) and LINDSTRÖM 2007.	17
Table 7: Average composition of bottom ash, cyclone ash and the finest ash fraction from the combustion of woody material (bark, wood chips and saw shavings) and straw (adapted from [OBERNBERGER 2001 (1)])	26
Table 8: Overview about methods for the assessment of ash melting and slagging.	29
Table 9: Raw materials used and number of samples investigated per fuel.	37
Table 10: Overview about organic and mineral additives used for pellets production.	38
Table 11 (Part A): Variation range of fuel properties of the investigated fuels (High-quality wood, low-quality wood, grain and hay).	39
Table 12: Overview of combustion units and their main characteristics.	42
Table 13: Overview of the experimental program and number of samples investigated either in combustion tests or analysed only. (R_{HQ} , R_{LQ} and R_{NW} are reference boilers for high quality wood, low quality wood and non-woody fuels respectively).	43
Table 14: Measuring instruments and principles.	44
Table 15: Overview about the experimental program conducted with wood pellets of test series I	45
Table 16: Overview about R-commands used for exploratory data analysis and multivariate calibration [R-packages].	54
Table 17: Classes according to ÖNORM EN 14961-1 assigned to the groups determined via k-means clustering.	61
Table 18: Variation of the ash composition – Average value (median) and spread (coefficient of quartile deviation c_{QD}) for the main constituents in bottom ash samples of different biomass fuels.	64
Table 19: Composition of bottom ashes from the combustion of low quality wood pellets with 2 % bark (LQ02) in different combustion units.	73
Table 20: Comparison of combustion conditions during ashing in a laboratory oven and in typical combustion appliances.	78
Table 21: Variation range of characteristic softening temperature (SOT) and flow temperature (FT) for different biomass fuels (without additive).	88
Table 22: Qualitative assessment of slag formation during combustion of biomass fuels in different boiler technologies	89
Table 23: Ash content, softening temperature (SOT) and flow temperature (FT) of the fuels shown in Figure 36 (a) and (b) respectively.	92
Table 24: Qualitative assessment of slag formation during combustion of various wood pellets in different combustion technologies. (adapted from FRIEDL 2006)	95
Table 25: Summary of fuel properties of the investigated pellets and comparison with reference fuels (pellets that formed slag are marked with bold letters).	97

Table 26: Slag formation during combustion of different wood pellet qualities for 4 different settings varying the grate cleaning interval (adapted from WOPIENKA 2008)	100
Table 27: Summary of fuel properties of the investigated pellets (pellets that formed slag are marked with bold letters)	103
Table 28: Concentration of particular elements in the investigated additives	106
Table 29: Qualitative assessment of slag formation during combustion of fuels with and without additives in different combustion technologies (adapted from CARVALHO 2007)	110
Table 30: Simplified fuel categories as to their elemental composition	115
Table 31: Overview about the main characteristics of the different boiler/stove technologies and qualitative description of slag formation and operating performance for the pellets that formed slag.	121
Table 32: Slag samples from selected wood fuels formed in different combustion units. (Pictures: FRIEDL 2006).....	123
Table 33: Overview about the main characteristics of the different boiler technologies and qualitative description of slag formation and operating performance for the investigated pellets.	124
Table 34: Performance of the investigated wood pellets fired in boiler L3 with original settings and reduced primary air supply (PAS shut).	127
Table 35: Combustion performance of straw and Miscanthus in boiler L8 using different grate cleaning settings.	130
Table 36: Problems and respective measures for the design of combustion technologies suited for slagging fuels	134
Table 37: Overview about elemental indices selected to be applied to own data set.....	136
Table 38: Overview about empirical equations selected to be applied to own data set.....	137
Table 39: Overview about parameters for variable selection (relative variance Var_{rel} , correlation coefficient to y cor_{xy} , model coefficients for full model E_b) and data-sets chosen for calculation (F , $R1$, $R2$).....	147
Table 40: Correlation coefficient for measured and predicted melting temperatures ($cor_{yy'}$), and RMSE for the calculated models (preferred model in bold letters).	148
Table 41: Basic information and comparison of test conditions of the investigated methods.....	155
Table 42: Comparison of the method output as well as experimental effort and objectiveness of the investigated methods.....	156
Table 43: Combustion relevant fuel properties of the investigated fuels (n.d.....not determined, n.o.....not observed)	186
Table 44: Elemental composition of the investigated fuels (n.d.....not determined, n.a.....not available).....	191

11 Annex III – List of figures

Figure 1: Basic principles of small-scale combustion technologies [ALAKANGAS 2002].	9
Figure 2: Basic types of grate systems including the typical range of capacity and fuel types applied, adopted from HARTMANN 2007.	10
Figure 3: Basic types of burner systems without a grate including the typical range of capacity and fuel types applied, adopted from HARTMANN 2007.	10
Figure 4: Innovative grate systems; (a) auger burner by Ligno Co. [BUCHEGGER 2011], (b) rotating grate by ETA Co. [ETA 2013] and (c) innovative rotary-grate by KWB Co. [KWB 2013].	11
Figure 5: Classification of elements according to their role and concentration in biomass (adapted from Mengel 1991)	12
Figure 6: Summary of release data gathered from literature for chlorine (a), potassium (b), sulphur (c) and zinc (d) at different temperatures. References: [I]...FRANDSEN 2005, [II]...FRANDSEN 2007, [III]...VAN LITH 2008, [IV]...KNUDSEN 2004, [V]...THY 2006 (1), [VI]...THY 2006 (2), [VII]...LANG 2006, [VIII]...WU 2011, [IX]...GILBE 2008 (1)	21
Figure 7: Aerosol formation during fixed-bed combustion of bark [OBERNBERGER 2001 (2)]	25
Figure 8: Presentation of different biomass samples for classification purposes (Group A: straw like fuel ashes, Group B: wood-type fuel ashes, Group C: high-alkali fuel ashes) [CAPABLO 2009] (a) and data-points representing biomass samples compared to melting curves [BOSTRÖM 2009] (b) in ternary diagrams.	32
Figure 9: Definition of characteristic temperatures according to DIN 51730 (H...height, r...base diameter)	33
Figure 10: Definition of characteristic temperatures according to ÖNORM CEN/TS 15370 (H...height, r...base diameter)	33
Figure 11: Experimental setup (a) and graphic response of the ACIRL-Test [KAHRAMAN 1998]	34
Figure 12: Basic principle of the CSIRO-Test [WALL 1998] (a) and TMA-Test [GUPTA 1998] (b), and graphic response of TMA-Test [GUPTA 2007] (c).	34
Figure 13: Conversion of STA curves to melt curve [HANSEN 1999]	35
Figure 14: Number of fuel samples representing a particular ash content.	40
Figure 15: Schematic drawing of the experimental setup with measurements points.	44
Figure 16: Ash sampling positions in boiler L1 and boiler L7.	47
Figure 17: Tukey boxplot with the characteristics of the data set. [FABER 2012]	50
Figure 18: Scoreplot and loadingplot of PC1 vs. PC2 (a)/(b), PC1 vs. PC3 (c)/(d) and PC2 vs. PC3 (e)/(f). Assignment of scores to different groups determined via kmeans-clustering (k=5) is marked with different colours	57
Figure 19: Dendrogram representing the distance of the investigated objects in the multi-dimensional space.	59
Figure 20: Comparison of major ash forming elements in fuel and bottom ash for spruce (bark-free), barley and Miscanthus.	63
Figure 21: Variability of the fraction of CaO (a), K ₂ O (b), P ₂ O ₅ (c) and SiO ₂ (d) in the fuel ash shown for different types of fuels.	65
Figure 22: Composition of bottom ash (BA) and ash from the heat exchanger (HE) from the combustion of wood pellets (a) and pellets of non-wood biomass (b).	66
Figure 23: Composition of ash (Ash) and slag (SL) from the combustion zone from the combustion of wood pellets with bark, low quality wood pellets and pellets made of maize (whole crop).	67
Figure 24: Variation of oxide fractions in ashes from one fuel sample fired in different combustion units for samples of wood, maize whole crop, Miscanthus and straw. Each fuel is presented in one row.	67
Figure 25: Variation of oxide fraction in combustion ashes. (Each data point is calculated from different ashes (fired in different combustion units) of the same fuel).	69
Figure 26: Residual fraction of chlorine (a), potassium (b), sulphur (c) and zinc (d) in the ash from the combustion in two different small-scale combustion units	71
Figure 27: Residual fractions of chlorine, potassium, sulphur and zinc in ashes from the combustion of wood pellets with 2 % bark (LQ02) in different combustion units.	72
Figure 28: Residual fractions of chlorine (a), potassium (b), sulphur (c) and zinc (d) in the bottom ash of different combustion units for different fuel classes determined via cluster analysis. (Woody and non-woody biofuels without additives are considered.)	75
Figure 29: Sum of oxides in samples of laboratory ashes at different temperatures (550 °C and 815 °C) and ashes from combustion tests in different types of boilers.	79

Figure 30 (Part 1): Fraction of ash forming oxides in laboratory ashes and ashes from combustion appliances burning wood pellets. Variation range for combustion ashes is marked as determined in chapter 5.2.3.	81
Figure 31: Remaining fractions of chlorine (a), potassium (b), sulphur (c) and zinc (d) in the ash from wood pellets combustion for laboratory ashes (550 °C and 815 °C) and ashes from combustion appliances.	83
Figure 32: Softening temperature (a) and flow temperature (b) for laboratory and boiler ashes from the combustion of woody and non-woody biomass. Accordance of values (continuous line) and limit of reproducibility (dashed line) are shown in addition.	85
Figure 33: Scoreplot (a) and loadingplot (b) of the first two principal components (main ash forming elements are considered as parameters, both fuel samples with and without additives are included)	85
Figure 34: Variation range of softening temperature (SOT) (a) and flow temperature (FT) (b) for different types of biomass.	88
Figure 35: Combustion zone in boiler L5 during/after the combustion of straw (a) and (b), maize whole crop (c) and (d) and after the combustion of Miscanthus (e).	90
Figure 36: Quantitative evaluation of slag formation from the combustion of different fuels in boiler L8 for standard grate cleaning settings (a) and more frequent grate cleaning intervals (b).	91
Figure 37: Elemental composition of the investigated fuels shown in Figure 36.	92
Figure 38: Slag particles after the combustion of larch in boiler L1 (a) and L4 (b) and spruce with ~5 % bark in boiler L1 (c) and L6 (d). [FRIEDL 2006]	96
Figure 39: Fractions of the main oxides in sum of ash forming elements for selected wood pellets. For HQ01 the variation range of all pure spruce samples investigated is marked.	98
Figure 40: Detail of the PCA-plot (PC1 vs. PC2) discussed in chapter 5.1 showing the wood pellets cluster. (Only investigated pellets are labelled.)	99
Figure 41: Slag formation in the burner pot for (a) LQ15 and (b) LQ19 (interval IV) [WOPIENKA 2008]	101
Figure 42: Slag samples from the combustion tests with interval IV [WOPIENKA 2008]	102
Figure 43: Fraction of slag in total combustion residues (interval IV) versus ash content (a) and Flow Temperature (b). [WOPIENKA 2008]	103
Figure 44: Fractions of the main oxides in sum of ash forming elements for the investigated wood pellets and the mixed biomass pellets. Wood pellets are ranked by increasing slag formation tendency.	104
Figure 45: Detail of the score-plot (PC1 vs. PC2) discussed in chapter 5.1 showing the wood pellets cluster. (Only investigated samples are labelled.)	105
Figure 46: SOT (a) and FT (b) for different straw samples with lime and Dollit TM	107
Figure 47: SOT (a) and FT (b) for fuel samples produced from one raw material with one Al-containing additive (mullite) and one Ca-containing additive (Lime).	107
Figure 48: Characteristic temperatures (SOT and FT) for two straw samples with different Mg- and Mg/Ca-additives (a) as well as different Ca- and Ca/Mg-additives.	108
Figure 49: SOT (a) and FT (b) for fuel samples produced with different Al-containing additives.	108
Figure 50: Slag formation of fuels with and without additives in boiler L8.	111
Figure 51: Fraction of largest slag particles after combustion of different fuels with and without additive. [CARVALHO 2007]	112
Figure 52: Elemental composition of the investigated Si-rich Miscanthus samples (Mip01, Mip02, Mip09) (a) and the P-rich fuels (wheat bran OTp03, maize whole crop MCp02 and MCp03, wood pellets with shredded maize HQ12) (b) .	116
Figure 53: Grate section of boiler L5 (a), L7 I (b) and L7 II (c) and slag formed in the respective boilers ((d) - (f)) after the combustion of MCp02. [CARVALHO 2007]	126
Figure 54: Bottom view of the grate area of boiler L3 with moving grate completely opened. (Pictures: FRIEDL 2006)	127
Figure 55: Temperatures in the combustion zone for the first 36 hours of the combustion test in boiler L3.	128
Figure 56: Fraction of slag agglomerates > 5.6 mm in total ash from the combustion of straw (STp03) applying different grate cleaning frequencies. (adapted from WOPIENKA 2007)	131
Figure 57: Fraction of slag that remained in the burner pot after 6 h of combustion when applying different grate cleaning intervals, i.e. 80 min. (I), 140 min. (II), 200 min. (III) and 360 min. (IV). Results are shown for fuels with minor slag formation tendency (a) and fuels that showed severe slag formation (b).	131
Figure 58: SOT (a) and FT (b) vs. the fraction of basic oxides. Colour of data points is related to Si/Al-ratio. Black: Si/Al > 30; Green: Si/Al < 30.	138
Figure 59: SOT (a) and FT (b) vs. B/A _(+P) . Colour of data points is related to Si/Al-ratio. Black: Si/Al > 30; Green: Si/Al < 30.	139

Figure 60: Softening temperature (SOT) vs. slag viscosity index S_R (a) and elemental ratio of $Si/(Ca+Mg)$ (b).....	140
Figure 61: Measured values for SOT vs. predicted values according to the equations of Bryers [BRYERS 1996] (a) using approach 1 (for $Si/Al \gg 1$) for ratios of 5-30 and (b) using approach 2 (for $Si/Al \sim 1$) for ratios of 5-30 for means of comparison.	141
Figure 62: Calculated values vs. measured values for SOT (a) and FT (b) calculated from different empirical equations [KOVITSKII 1975, REISINGER 1993, FRIEDL 2004, HARTMANN 2000].	142
Figure 63: Slag formed during combustion test related to the respective $B/A_{(+P)}$ -value for wood and wood mixtures (a) and different non-woody biomass fuels (b).....	142
Figure 64: Qualitative assessment of slag formed during combustion tests vs. $B/A_{(+P)}$ -values for woody (a) and non-woody (b) biomass.....	143
Figure 65: Characteristic temperatures (SOT (a) and FT(b)) vs. $B/A_{(+P)}$ index for straw pellets with and without additives.....	145
Figure 66: Simplified drawing of a SOT- $B/A_{(+P)}$ -characteristic showing typical ranges for various raw materials. Arrows show the direction to which index-values are shifted when using particular types of additives.	145
Figure 67: Performance of SOT-model (a)-(b) and FT-model (c)-(d) (fuel-data set R2, 1 PLS component)	148

12 Annex IV – Properties of fuel and ash samples

Table 43: Combustion relevant fuel properties of the investigated fuels (n.d.....not determined, n.o.....not observed)

Fuel ID	Fuel description	LHV MJ/kg (d.b.)	w % (d.b.)	a % (d.b.)	VM % (d.b.)	A (SOT) °C	B (SPT) °C	C (HT) °C	D (FT) °C
High quality wood									
HQ01	Spruce, saw dust	17.28	13.1	2.43	80.3	904	n.o.	1258	1295
HQ02	Spruce, saw dust (1 % starch)	17.52	12.7	2.15	80.8	747	n.o.	1000	1140
HQ03	Spruce, saw dust (1 % starch)	17.67	11.6	2.43	80.4	1136	n.o.	1254	1317
HQ04	Spruce, saw dust	17.63	11.3	1.13	83.8	747	758	775	790
HQ05	Spruce, saw dust	15.51	12.0	8.03	77.6	> 1400	> 1400	> 1400	> 1400
HQ06	Spruce, saw dust (1 % starch)	17.20	12.4	3.20	79.5	1185	n.o.	1220	1249
HQ07	Spruce, saw dust (1 % starch)	16.91	10.6	2.73	78.5	1146	n.o.	1202	1263
HQ08	Spruce, saw dust (2 % starch)	17.46	12.9	2.38	80.0	720	920	950	990
HQ09	Spruce, saw dust (5 % starch)	17.49	12.8	2.46	80.2	690	n.o.	1200	1230
HQ10	Spruce, saw dust (1 % Maize meal)	17.18	10.2	3.51	80.0	1030	n.o.	1270	1360
HQ11	Spruce, saw dust (2 % Maize meal)	17.73	n.d.	1.81	83.2	750	770	780	790
HQ12	Spruce, saw dust (5 % Maize meal)	18.87	7.6	0.29	84.0	1360	n.o.	1460	1470
HQ13	Spruce, saw dust (1 % Rye meal)	18.56	7.1	0.26	84.2	1390	n.o.	1440	1450
HQ14	Spruce, saw dust (2 % Rye meal)	18.72	9.8	0.23	84.1	1340	n.o.	1430	1440
HQ15	Spruce, saw dust (5 % Rye meal)	18.95	6.9	0.36	84.4	1370	n.o.	1420	1430
HQ16	Spruce (wood shavings)	18.98	7.4	0.36	84.7	1350	n.o.	1420	1430
HQ17	Spruce (grinding dust)	18.79	9.5	0.25	85.1	1370	n.o.	1460	1470
HQ18	Pine (sawdust)	18.81	7.9	0.32	84.9	1380	n.o.	1440	1450
HQ19	Larch (sawdust)	18.74	8.0	0.26	84.5	1370	n.o.	1420	1430
Low quality wood									
LQ01	Spruce, saw dust + 2 % bark	18.66	8.2	0.34	83.6	1359	n.o.	1445	1460
LQ02	Spruce, saw dust + 5 % bark	18.83	7.5	0.59	83.5	1347	n.o.	1456	1460
LQ03	wood pellets from the market (no info)	18.65	7.6	0.51	n.d.	1161	1185	1195	1203
LQ04	wood pellets from the market (no info)	n.d.	n.d.	0.37	n.d.	1313	n.o.	n.o.	n.o.
LQ05	wood pellets from the market (no info)	18.62	7.3	0.90	83.9	n.d.	n.d.	n.d.	n.d.
LQ08	wood pellets from the market (no info)	18.78	7.0	0.32	83.9	930	n.o.	1450	1450

Table 43 (continuation): Combustion relevant fuel properties of the investigated fuels (n.d.....not determined, n.o.....not observed)

Fuel ID	Fuel description	LHV MJ/kg (d.b.)	w % (d.b.)	a % (d.b.)	VM % (d.b.)	A (SOT) °C	B (SPT) °C	C (HT) °C	D (FT) °C
LQ09	wood pellets from the market (softwood, saw dust and shavings)	18.96	8.4	0.26	83.9	1230	n.o.	1350	1360
LQ10	wood pellets from the market (Saw dust from pine, larch, fir)	19.14	8.6	0.33	84.3	1230	n.o.	1250	1270
LQ11	wood pellets from the market (spruce saw dust and shavings)	18.91	5.6	0.34	83.7	1420	1460	1460	1460
LQ13	wood pellets from the market (coniferous, saw dust)	19.00	8.5	0.36	84.0	1020	n.o.	1410	1430
LQ14	wood pellets from the market (spruce, pine, saw dust)	19.20	4.8	0.32	83.3	1320	n.o.	1440	1450
LQ15	wood pellets from the market (beech, saw dust)	18.19	7.6	2.06	81.2	1180	n.o.	1230	1230
LQ16	wood pellets from the market (birch, chipped wood)	18.84	n.d.	0.55	85.2	1400	n.o.	1460	1460
LQ17	wood pellets from the market (campeche wood, saw dust and bark)	18.69	8.4	1.28	82.8	1120	n.o.	1250	1250
LQ18	wood pellets from the market (oak, pine, saw dust)	18.66	7.5	0.67	80.8	1390	n.o.	1430	1430
LQ19	wood pellets from the market (used wood, saw dust)	18.86	6.3	0.93	81.4	1290	n.o.	1310	1330
LQ20	wood pellets from the market (no info)	n.d.	n.d.	0.70	n.d.	1360	> 1460	> 1460	> 1460
Grain									
GRp01	10 % Barley / 90 % Wheat	17.28	13.1	2.43	80.3	904	n.o.	1258	1295
GRa01	50 % Barley / 50 % Wheat, 2 % Lime	17.52	12.7	2.15	80.8	747	n.o.	1000	1140
GRp02	Brewing barley	17.67	11.6	2.43	80.4	1136	n.o.	1254	1317
GRp03	Maize	17.63	11.3	1.13	83.8	747	758	775	790
GRa02	10 % Barley / 90 % Wheat, 6 % Lime	15.51	12.0	8.03	77.6	> 1400	> 1400	> 1400	> 1400
GRp04	Grain cleaning residues (95 % barley/5 %wheat)	17.20	12.4	3.20	79.5	1185	n.o.	1220	1249
GRp05	Spring barley	16.91	10.6	2.73	78.5	1146	n.o.	1202	1263
GRa03	Wheat, 2 % Lime	17.46	12.9	2.38	80.0	720	920	950	990
GRa04	Barley, 2 % Lime	17.49	12.8	2.46	80.2	690	n.o.	1200	1230
GRp06	Brewing barley	17.18	10.2	3.51	80.0	1030	n.o.	1270	1360
GRp07	Maize	17.73	n.d.	1.81	83.2	750	770	780	790
Hay									
HAp02	Hay (mixture of charges)	16.21	n.d.	11.20	71.2	1070	1170	1230	1260
HAp03	Hay (mixture of charges)	16.78	n.d.	9.80	74.4	1150	1210	1270	1320
HAp04	Hay (mixture of charges)	16.90	7.5	7.40	73.1	1140	1160	1200	1230
HAp05	Hay (one charge)	16.94	13.1	9.60	71.9	820	1050	1080	1180
HAp06	Hay (one charge)	17.74	16.5	6.00	74.6	870	1140	1160	1180
HAp07	Hay (one charge)	17.22	17.8	7.10	74.2	840	1070	1170	1210

Table 43 (continuation): Combustion relevant fuel properties of the investigated fuels (n.d.....not determined, n.o.....not observed)

Fuel ID	Fuel description	LHV MJ/kg (d.b.)	w % (d.b.)	a % (d.b.)	VM % (d.b.)	A (SOT) °C	B (SPT) °C	C (HT) °C	D (FT) °C
Maize whole crop									
MCp02	Maize whole crop	17.32	11.31	3.37	81.7	n.d.	n.d.	n.d.	n.d.
MCp03	Maize whole crop	17.48	11.65	3.39	80.2	910	930	960	990
MCa05	Maize whole crop, 2 % Dollit™	16.76	10.19	6.31	78.9	n.d.	n.d.	n.d.	n.d.
MCp04	Maize whole crop	17.75	13.5	2.83	81.3	1000	1100	1110	1120
Miscanthus									
MIp01	Miscanthus	17.73	8.59	3.05	80.8	n.d.	n.d.	n.d.	n.d.
MIp02	Miscanthus	17.83	8.68	3.26	82.9	1010	>1400	>1400	>1400
MIa01	Miscanthus, Dollit™	17.43	8.54	5.02	80.2	n.d.	n.d.	n.d.	n.d.
MIa02	Miscanthus, bauxite	17.10	8.59	6.62	79.6	n.d.	n.d.	n.d.	n.d.
MIp03	Miscanthus	18.01	9.3	2.53	80.5	1010	1060	1150	1240
MIp04	Miscanthus	17.97	7.0	2.27	80.3	820	1080	1200	1240
MIp05	Miscanthus	17.96	8.1	3.19	80.0	1060	1110	1210	1260
MIp06	Miscanthus	18.07	7.0	1.99	81.7	870	970	1110	1150
MIp07	Miscanthus	17.99	7.6	2.40	81.5	850	970	1100	1170
MIp08	Miscanthus	17.99	7.9	2.10	81.0	880	950	1090	1170
MIp09	Miscanthus	18.15	7.7	2.90	82.3	1172	n.o.	1256	1260
Other Biomass and mixed pellets									
OTp02	Maize residues	17.54	7.6	2.40	78.2	1100	1163	1200	1270
OTp03	Bran	17.98	13.7	5.70	n.d.	670	860	890	940
OTp04	Rape seed cake	n.d.	n.d.	n.d.	n.d.	860	n.o.	1170	1170
OTp05	Giant reed	17.87	7.1	4.90	75.8	893	1048	1126	1169
OTp07	Pruning	n.d.	8.4	2.80	n.d.	795	> 1450	> 1450	> 1450
OTp09	Sorghum bicolor	17.46	7.4	6.30	75.3	990	n.o.	1070	1080
Mx01	Spruce (saw dust) + maize residues	18.36	6.3	1.13	80.7	1400	n.o.	1460	1460
Mx02	Spruce (saw dust)+ straw	18.76	7.9	0.83	82.8	1020	n.o.	1410	1430
Straw									
STa02	Straw with Dollit™	16.79	7.8	7.34	75.6	n.d.	n.d.	n.d.	n.d.
STa03	Straw with bauxite	17.02	7.7	7.11	75.4	n.d.	n.d.	n.d.	n.d.
STa06	Straw with bauxite	16.69	7.1	9.46	71.7	820	> 1400	> 1400	> 1400

Table 43 (continuation): Combustion relevant fuel properties of the investigated fuels (n.d.....not determined, n.o.....not observed)

Fuel ID	Fuel description	LHV MJ/kg (d.b.)	w % (d.b.)	a % (d.b.)	VM % (d.b.)	A (SOT) °C	B (SPT) °C	C (HT) °C	D (FT) °C
STa07	Straw, 5 % Lime	17.11	8.4	8.19	74.0	994	n.o.	1151	1170
STa08	Straw, 3 % Dollit™	16.67	9.3	7.77	73.2	1258	n.o.	1286	1301
STa11	Straw, 5 % bauxite	16.86	6.6	8.29	71.6	890	> 1450	> 1450	> 1450
STa12	Straw, 0.6 % Lime	n.d.	n.d.	n.d.	n.d.	1030	1060	1080	1120
STa13	Straw, 1.8 % Lime	n.d.	n.d.	n.d.	n.d.	1160	n.o.	1180	1190
STa14	Straw, 3.1 % carbonate of Lime	n.d.	n.d.	n.d.	n.d.	1110	n.o.	1150	1180
STa15	Straw, 3 % Dollit™	n.d.	n.d.	n.d.	n.d.	1130	n.o.	1160	1250
STa16	Straw, 5.8 % Dollit™	n.d.	n.d.	n.d.	n.d.	1280	n.o.	1290	1300
STa17	Straw, 0.7 % mullite	n.d.	n.d.	n.d.	n.d.	1160	1140	1160	1200
STa18	Straw, 2.1 % mullite	n.d.	n.d.	n.d.	n.d.	1280	1305	1320	1340
STa19	Straw, 1.4 % AISiH™	n.d.	n.d.	n.d.	n.d.	920	1250	1380	~1400
STa20	Straw, 5.8 % bentonite	n.d.	n.d.	n.d.	n.d.	1100	1150	1200	1270
STa21	Straw, 11.5 % bentonite	n.d.	n.d.	n.d.	n.d.	1110	1190	1250	1310
STa22	Straw, 4.5 % Lime	n.d.	n.d.	n.d.	n.d.	1110	n.o.	1308	1370
STa23	Straw, 2 % Dollit™	n.d.	n.d.	n.d.	n.d.	860	1086	1120	1140
STa24	Straw, 4 % Dollit™	n.d.	n.d.	n.d.	n.d.	1150	n.o.	1210	1220
STa25	Straw, 2 % carbonate of Lime	n.d.	n.d.	n.d.	n.d.	866	992	1111	1135
STa26	Straw, 1.4 % mullite	n.d.	n.d.	n.d.	n.d.	956	n.o.	1280	1290
STa27	Straw, 2.8 % mullite	n.d.	n.d.	n.d.	n.d.	1400	n.o.	1410	1420
STa28	Straw, 4.2 % AISiH™	n.d.	n.d.	n.d.	n.d.	937	n.o.	1430	1440
STa29	Straw, mullite+ AISiH™ (0.25/0.75)	n.d.	n.d.	n.d.	n.d.	1400	n.o.	1433	1445
STa30	Straw, mullite+ AISiH™ (0.6/0.4)	n.d.	n.d.	n.d.	n.d.	1393	1428	1430	1430
STa31	Straw, 11.2 % Sialin™	n.d.	n.d.	n.d.	n.d.	1160	1320	1400	1430
STa32	Straw, 1.8 % lime	n.d.	n.d.	n.d.	n.d.	1080	1120	1170	1190
STa33	Straw, 2.6 % (Dollit™+mullite 1/1)	n.d.	n.d.	n.d.	n.d.	1190	1200	1210	1210
STa34	Straw, 4.3 % (Dollit™+mullite 1/1)	n.d.	n.d.	n.d.	n.d.	1187	n.o.	1256	1264
STp01	Straw	17.36	8.8	5.39	76.2	n.d.	n.d.	n.d.	n.d.
STp02	Straw	15.97	n.d.	12.90	n.d.	n.d.	n.d.	n.d.	n.d.
STp03	Straw	17.32	7.9	5.71	74.8	800	890	1060	1080
STp04	Straw	16.99	7.3	6.50	74.3	840	850	1030	1060

Table 43 (continuation): Combustion relevant fuel properties of the investigated fuels (n.d.....not determined, n.o.....not observed)

Fuel ID	Fuel description	LHV	w	a	VM	A (SOT)	B (SPT)	C (HT)	D (FT)
		MJ/kg (d.b.)	% (d.b.)	% (d.b.)	% (d.b.)	°C	°C	°C	°C
STp05	Straw	17.18	n.d.	6.30	75.4	n.d.	n.d.	n.d.	n.d.
STp06	Straw	17.27	n.d.	5.10	75.6	n.d.	n.d.	n.d.	n.d.
STp07	Straw	17.60	n.d.	5.67	n.d.	820	980	1070	1080
STp08	Straw	n.d.	n.d.	n.d.	n.d.	814	n.o.	1065	1084
STp09	Straw	n.d.	n.d.	n.d.	n.d.	726	n.o.	1046	1059
STp10	Straw	n.d.	n.d.	n.d.	n.d.	786	n.o.	924	1022
STp11	Straw	n.d.	n.d.	n.d.	n.d.	772	n.o.	893	1024

Table 44: Elemental composition of the investigated fuels (n.d.....not determined, n.a.....not available)

		C	H	N	Al	Ca	Cl	Fe	K	Mg	Mn	Na	P	S	Si	Ti	Zn
		in % (d.b)			in mg/kg (d.b.)												
High quality wood																	
HQ01	Spruce, saw dust	50.7	5.80	0.10	25	883	21	30	348	119	96	10	35	42	37	n.d.	10
HQ02	Spruce, saw dust (1 % starch)	50.8	5.88	0.13	25	856	22	30	337	117	92	10	35	41	32	n.d.	10
HQ03	Spruce, saw dust (1 % starch)	50.6	5.88	0.12	25	838	17	24	339	114	94	10	32	37	23	n.d.	11
HQ04	Spruce, saw dust	51.5	5.73	0.11	27	853	17	18	333	120	103	10	34	39	30	n.d.	9
HQ05	Spruce, saw dust	51.2	5.85	0.15	25	831	33	10	390	140	134	11	38	44	56	n.d.	10
HQ06	Spruce, saw dust (1 % starch)	51.3	5.94	0.10	25	837	16	18	323	119	107	10	40	38	27	n.d.	8
HQ07	Spruce, saw dust (1 % starch)	51.4	5.95	0.13	15	846	16	13	331	122	102	10	41	43	13	n.d.	8
HQ08	Spruce, saw dust (2 % starch)	51.4	5.97	0.10	15	847	22	17	319	120	102	10	37	39	14	n.d.	8
HQ09	Spruce, saw dust (5 % starch)	51.0	5.60	0.12	15	786	25	13	331	106	96	10	41	39	7	n.d.	8
HQ10	Spruce, saw dust (1 % Maize meal)	51.2	5.73	0.14	15	818	21	17	375	124	95	10	69	49	48	n.d.	8
HQ11	Spruce, saw dust (2 % Maize meal)	50.0	5.66	0.19	25	916	17	23	439	201	88	10	111	68	29	n.d.	9
HQ12	Spruce, saw dust (5 % Maize meal)	49.8	5.71	0.21	15	771	46	16	555	178	89	10	238	110	15	n.d.	9
HQ13	Spruce, saw dust (1 % Rye meal)	49.8	5.56	0.14	15	821	23	15	340	119	99	10	51	49	13	n.d.	8
HQ14	Spruce, saw dust (2 % Rye meal)	51.0	5.78	0.15	15	814	37	27	391	126	96	10	75	62	8	n.d.	8
HQ15	Spruce, saw dust (5 % Rye meal)	50.7	5.86	0.21	15	822	42	15	437	137	98	10	101	81	9	n.d.	9
HQ16	Spruce (wood shavings)	51.5	5.95	0.13	28	888	22	11	298	116	103	10	26	41	36	n.d.	8
HQ17	Spruce (grinding dust)	51.3	5.93	0.30	25	895	17	9	268	112	110	10	20	80	15	n.d.	9
HQ18	Pine (sawdust)	51.5	5.94	0.10	15	922	40	7	365	178	183	10	50	53	20	n.d.	8
HQ19	Larch (sawdust)	51.1	5.91	0.11	30	764	43	27	437	158	99	15	22	44	77	n.d.	5
Low quality wood																	
LQ01	Spruce, saw dust + 2 % bark	50.9	5.91	0.12	50	1112	20	54	379	146	107	12	45	47	112	n.d.	12
LQ02	Spruce, saw dust + 5 % bark	51.1	5.99	0.17	120	1474	26	101	470	190	119	27	58	58	269	n.d.	16
LQ03	wood pellets from the market (no info)	n.d.	n.d.	n.d.	47	930	35	56	450	109	124	27	46	53	217	n.d.	13
LQ04	wood pellets from the market (no info)	n.d.	n.d.	n.d.	45	720	105	37	714	213	59	17	28	84	125	n.d.	8
LQ05	wood pellets from the market (no info)	n.d.	n.d.	n.d.	360	1741	70	344	569	440	202	89	38	101	1355	n.d.	n.d.
LQ08	wood pellets from the market (no info)	n.d.	n.d.	n.d.	15	840	n.d.	16	467	126	83	27	63	57	173	n.d.	10
LQ09	wood pellets from the market (softwood, saw dust and shavings)	51.3	6.27	<0.10	50	712	46	71	399	126	163	23	50	53	240	11	12

Table 44 (continuation): Elemental composition of the investigated fuels (n.d.....not determined, n.a.....not available)

		C	H	N	Al	Ca	Cl	Fe	K	Mg	Mn	Na	P	S	Si	Ti	Zn
		in % (d.b)			in mg/kg (d.b.)												
LQ10	wood pellets from the market (Saw dust from pine, larch, fir)	53.3	6.30	<0.10	57	751	22	66	400	144	134	17	58	69	371	16	9
LQ11	wood pellets from the market (spruce saw dust and shavings)	49.6	6.18	<0.11	12	451	28	15	218	67	107	6	40	32	206	2	7
LQ13	wood pellets from the market (coniferous, saw dust)	50.0	6.09	<0.11	38	789	53	301	340	112	87	13	39	183	270	7	8
LQ14	wood pellets from the market (spruce, pine, saw dust)	53.2	6.39	<0.10	62	875	18	78	430	136	108	23	49	55	274	14	13
LQ15	wood pellets from the market (beech, saw dust)	48.7	5.93	0.23	840	2780	24	581	1440	413	103	153	87	116	3340	103	9
LQ16	wood pellets from the market (birch, chipped wood)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
LQ17	wood pellets from the market (campeche wood, saw dust and bark)	52.5	6.17	<0.10	470	1830	21	292	580	267	194	65	49	72	2440	62	15
LQ18	wood pellets from the market (oak, pine, saw dust)	50.1	5.96	0.39	200	1550	25	73	656	201	47	43	41	151	391	9	11
LQ19	wood pellets from the market (used wood, saw dust)	50.1	6.06	0.20	120	1740	166	300	662	265	100	116	55	112	484	38	18
LQ20	wood pellets from the market (no info)	n.d.	n.d.	n.d.	80	1140	24	56	857	143	86	10	57	96	341	11	5
Grain																	
GRp01	10 % Barley / 90 % Wheat	41.5	6.61	2.00	11	740	980	40	4800	1200	30	33	3960	1500	1200	82	27
GRa01	50 % Barley / 50 % Wheat, 2 % lime	41.4	6.56	2.27	10	540	920	45	4500	1400	37	24	3950	1700	600	64	23
GRp02	Brewing barley	41.7	6.63	1.94	36	460	1500	54	5500	1300	18	117	4190	1400	1300	29	29
GRp03	Maize	45.5	6.76	1.52	< 10	67	605	26	3260	1020	6	< 50	2720	1100	< 200	11	22
GRa02	10 % Barley / 90 % Wheat, 6 % lime	46.0	5.70	2.45	25	3809	770	50	4228	1229	30	< 50	3614	1657	232	24	32
GRp04	Grain cleaning residues (95 % barley/5 %wheat)	46.1	5.60	2.26	29	575	1408	65	5512	1178	17	66	3904	1525	2826	118	27
GRp05	Spring barley	45.5	5.63	2.23	6	432	1388	44	5744	1244	17	77	3715	1377	2754	48	20
GRa03	Wheat, 2 % lime	46.2	6.21	2.40	8	581	n.a.	75	6450	1469	43	13	4260	1463	221	2	31
GRa04	Barley, 2 % lime	45.9	6.00	1.99	11	356	946	61	5447	1402	15	61	3539	1614	1643	16	34
GRp06	Brewing barley	45.3	6.11	1.63	14	479	1412	58	6623	1467	18	58	4180	1304	3373	43	27
GRp07	Maize	46.4	6.29	1.35	< 10	61	394	25	3825	1109	6	< 6	2873	1005	159	4	20

Table 44 (continuation): Elemental composition of the investigated fuels (n.d.....not determined, n.a.....not available)

		C	H	N	Al	Ca	Cl	Fe	K	Mg	Mn	Na	P	S	Si	Ti	Zn
		in % (d.b)			in mg/kg (d.b.)												
Hay																	
HAp02	Hay (mixture of charges)	44.7	5.37	1.24	4040	7100	3330	1950	17400	2370	254	600	1560	1320	17300	707	31
HAp03	Hay (mixture of charges)	42.2	5.52	1.29	6480	4210	2550	2280	10700	658	245	1530	1440	1330	36400	724	32
HAp04	Hay (mixture of charges)	45.9	5.72	1.07	2280	6300	1090	936	10200	2460	103	1200	2460	1340	12600	249	26
HAp05	Hay (one charge)	44.6	5.72	1.65	550	6030	2250	1540	20700	1710	335	472	2440	1730	12900	302	42
HAp06	Hay (one charge)	46.2	5.91	0.90	610	6070	3470	517	15800	1320	85	199	1450	1010	5770	128	20
HAp07	Hay (one charge)	45.2	5.81	1.00	630	3840	1380	916	12800	1140	208	487	1610	1260	13200	234	27
Maize whole crop																	
MCp02	Maize whole crop	47.5	5.94	1.20	350	1783	683	312	5088	1471	24	103	1991	1056	4695	62	21
MCp03	Maize whole crop	45.9	6.25	0.89	130	936	1024	123	7841	1065	15	26	1999	870	3613	126	17
MCa05	Maize whole crop, 2 % Dollit™	44.6	6.00	0.76	270	8098	928	197	8126	4764	20	47	1924	814	3802	162	19
MCp04	Maize whole crop	45.3	6.32	1.12	110	1213	645	114	4812	1273	15	42	1804	986	3379	32	18
Miscanthus																	
MIp01	Miscanthus	48.9	5.76	0.23	180	1019	253	157	2608	419	37	152	300	352	9786	27	12
MIp02	Miscanthus	47.3	5.99	0.24	81	1619	214	93	987	988	47	25	318	342	9829	126	13
MIa01	Miscanthus, Dollit™	46.9	5.77	0.17	300	9302	125	159	2100	4962	68	52	229	376	9096	143	11
MIa02	Miscanthus, bauxite	47.3	5.65	0.09	11600	1423	232	785	1948	697	46	52	249	335	9260	977	11
MIp03	Miscanthus	47.8	5.97	0.22	78	1327	650	101	3140	721	34	34	194	378	7440	38	8
MIp04	Miscanthus	48.9	5.81	0.22	53	1104	647	87	3533	468	52	55	479	462	5533	11	14
MIp05	Miscanthus	48.5	5.89	0.25	130	1420	453	136	2550	632	45	28	262	413	8400	75	11
MIp06	Miscanthus	48.7	6.05	0.23	56	807	521	79	3570	287	56	25	560	391	4910	13	11
MIp07	Miscanthus	51.0	6.07	0.19	57	1240	486	79	3490	646	25	19	168	476	5990	59	n.a.
MIp08	Miscanthus	51.0	6.13	0.29	76	1130	603	109	3700	436	52	33	423	448	4570	28	n.a.
MIp09	Miscanthus	48.3	5.91	0.28	520	3580	202	642	1490	1410	33	91	282	521	5460	88	21
Other Biomass and mixed pellets																	
OTp02	Maize residues	41.1	6.27	1.46	62	414	2885	72	8516	288	8	< 50	394	369	1147	249	11
OTp03	Bran	46.4	6.08	3.04	35	1070	920	142	15100	3520	118	554	9950	2390	889	10	76
OTp04	Rape seed cake	50.5	6.76	5.15	10	6850	210	86	12000	4590	61	21	10100	6240	103	1	52
OTp05	Giant reed	47.3	5.83	0.74	210	2490	2632	1090	8800	1530	32	63	955	1800	9050	42	41
OTp07	Pruning	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 44 (continuation): Elemental composition of the investigated fuels (n.d.....not determined, n.a.....not available)

		C	H	N	Al	Ca	Cl	Fe	K	Mg	Mn	Na	P	S	Si	Ti	Zn
		in % (d.b)			in mg/kg (d.b.)												
OTp09	Sorghum bicolor	n.d.	n.d.	n.d.	n.d.	n.d.	3390	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1100	n.d.	n.d.	n.d.
Mx01	Spruce (saw dust) + maize residues	49.0	6.11	0.16	38	764	1020	45	3320	175	72	25	197	162	350	15	13
Mx02	Spruce (saw dust) + straw	49.7	6.12	0.37	40	1130	276	43	1290	176	105	30	80	147	1370	14	12
Straw																	
STa02	Straw with Dollit™	46.7	5.63	0.41	440	7833	1347	387	7416	3686	30	106	481	716	12782	76	3
STa03	Straw with bauxite	46.5	5.77	0.39	1840	1901	2056	448	6842	540	23	90	531	802	13196	416	3
STa06	Straw with bauxite	44.7	5.85	0.35	10000	2407	4157	696	13255	724	37	54	520	550	13287	774	4
STa07	Straw, 5 % lime	45.1	6.13	0.63	120	10328	2027	107	15630	3809	13	81	405	1195	8415	701	8
STa08	Straw, 3 % Dollit™	46.7	5.11	0.55	120	10925	1866	108	14590	4415	13	67	411	1132	8884	103	6
STa11	Straw, 5 % bauxite	45.4	5.73	0.49	10500	2180	2480	845	11400	655	30	50	478	746	11900	1060	6
STa12	Straw, 0.6 % lime	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STa13	Straw, 1.8 % lime	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STa14	Straw, 3.1 % carbonate of lime	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STa15	Straw, 3 % Dollit™	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STa16	Straw, 5.8 % Dollit™	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STa17	Straw, 0.7 % mullite	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STa18	Straw, 2.1 % mullite	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STa19	Straw, 1.4 % AISiH™	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STa20	Straw, 5.8 % bentonite	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STa21	Straw, 11.5 % bentonite	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STa22	Straw, 4.5 % lime	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STa23	Straw, 2 % Dollit™	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STa24	Straw, 4 % Dollit™	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STa25	Straw, 2 % carbonate of lime	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STa26	Straw, 1.4 % mullite	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STa27	Straw, 2.8 % mullite	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STa28	Straw, 4.2 % AISiH™	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STa29	Straw, mullit+ AISiH™ (0.25/0.75)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STa30	Straw, mullit+ AISiH™ (0.6/0.4)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STa31	Straw, 11.2 % Sialin™	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 44 (continuation): Elemental composition of the investigated fuels (n.d.....not determined, n.a.....not available)

		C	H	N	Al	Ca	Cl	Fe	K	Mg	Mn	Na	P	S	Si	Ti	Zn
		in % (d.b)			in mg/kg (d.b.)												
STa32	Straw, 1.8 % lime	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STa33	Straw, 2.6 % (Dollit™+mullite 1/1)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STa34	Straw, 4.3 % (Dollit™+mullite 1/1)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STp01	Straw	47.0	5.78	0.62	1050	2639	998	837	7752	698	40	229	431	896	13732	170	4
STp02	Straw	44.9	5.27	0.45	2380	2713	1235	2708	8273	596	91	682	526	847	29152	397	8
STp03	Straw	47.3	5.80	0.66	230	2507	1720	148	14040	811	21	90	716	1008	10620	102	5
STp04	Straw	48.5	5.99	0.41	210	3740	5120	152	15700	948	34	477	696	898	11200	52	n.d.
STp05	Straw	46.5	5.59	0.39	390	2250	1120	167	6380	633	29	73	673	534	20100	n.d.	6
STp06	Straw	46.8	5.76	0.52	130	2570	574	85	8490	689	21	33	459	676	14600	n.d.	7
STp07	Straw	0.0	0.00	0.00	110	3237	2905	101	14791	1026	37	190	411	886	12340	n.d.	4
STp08	Straw	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STp09	Straw	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STp10	Straw	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
STp11	Straw	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

