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Combustion Properties of Biomass Residues Rich in Phosphorus

Patrycja Piotrowska

Academic Dissertation

Laboratory of Inorganic Chemistry

Patrycja Piotrowska

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Institute of Environmental Engineering/Energy Engineering

Faculty of Environmental Protection and Engineering

Czestochowa University of Technology

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Laboratory of Inorganic Chemistry
Process Chemistry Centre
Department of Chemical Engineering
Åbo Akademi University

Supervisor

Professor Mikko Hupa
Åbo Akademi University

Co -supervisors

Doctor Maria Zevenhoven
Åbo Akademi University

and

Docent Edgardo Coda Zabetta
Foster Wheeler Energia Oy

Opponent and reviewer

Professor Peter Ashman
The University of Adelaide

Reviewer

Professor Britt-Marie Steenari
Chalmers University of Technology

Preface

The work presented in this thesis was carried out during 2007-2011 at the Laboratory of Inorganic Chemistry at Åbo Akademi University as a part of the activities of the Process Chemistry Centre that has been designated since the year 2000 a Centre of Excellence by the Academy of Finland, 2000-2011.

Sweden, while spruce bark samples from the Södra Cell plant at Mönsterås Bruk in Sweden were supplied by Umeå University.

I would like to express my deepest gratitude to my supervisors Professor Mikko Hupa, Docent Edgardo Coda Zabetta, and Dr Maria Zevenhoven, for their expertise, encouragement, and advice. But most of all I want to thank them for their tolerance of my individuality. I was always grateful for being able to call myself their student.

During these five years I have learnt that life is a matter of taking opportunities we are given and about the choices we make. Thanks to Professor Wojciech Nowak (*Częstochowa University of Technology*) and the encouragement of my father, I had an opportunity in 2006 to meet Docent Edgardo Coda Zabetta. This great person started it all. I am grateful for the opportunity he gave me and for all the words which not only once showed me a light to follow and not only in science. You are one of the most inspiring people I know.

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This scientific journey of working on a PhD is not always pleasant but it is not supposed to be so. I was thrown into deep water in the first couple of months of my studies. To be

involved in the first project was both a challenge and pain, and for both I am grateful. Thanks to the collaboration with Professor Lars-Erik Åmand and Dr Kent Davidsson (*Chalmers University of Technology*), Dr Vesna Barišić and Docent Edgardo Coda Zabetta (*Foster Wheeler Energia Oy*), I gained an extensive foundation for my knowledge on fluidized beds and ash-related problems. Thank you for teaching me and allowing me to be the first author of two journal articles.

I would like to also acknowledge the co-operation with *Delft University of Technology* (Professor A. H. M. Verkooijen, Dr Wiebren de Jong, Dr Jacopo Giuntoli). Thanks to which I had an opportunity to perform all different type of laboratory studies with two additional fuel samples so perfectly fitting the objective of my work. This joint project showed me the vast scope of the complex field of fuel characterization, and how much there is to be learnt. At this stage I would like to also acknowledge two people not mentioned earlier but who where strongly involved in this collaboration: Dr Esperanza Monedero Villalba (*Universidad de Castilla-La Mancha*) and Dr Patrik Yrjas (*Åbo Akademi University*). Thank you for the time and all the discussions we had, which were not only related to this project. Your support when I was going through the PhD journey is much appreciated.

I would like to thank to Professor Mikko Hupa *(Åbo Akademi University)* and Professor Marcus Öhman (*Luleå University of Technology*) for initiating my exchange visit to Umeå University. I would like to thank Professor Dan Boström and Dr Christoffer Boman (*Umeå University*) for giving me the opportunity to go through this invaluable experience of being a part of ETPC and their hospitability. Without Alejandro Grimm (*Luleå University of Technology*) and Nils Skoglund (*Umeå University*) this visit would not have turned out to be so successful and efficient. The collaboration between these three Universities resulted in two publications enclosed in this thesis and hopefully other to come. It was a great lesson to me and I am grateful for your readiness to share your knowledge with an outsider.

I would like to also mention people who with no particular benefit to themselves showed their interest and cleared my thoughts in the first months of my PhD when my path was not yet very clear: Dr H. M. Londo (*Energy Research Centre of the Netherlands*), Tom Miles (*T R Miles Technical Consultants, Inc*), Dr Mikael Forsén (*Stora Enso*), Dr Johan Werkelin (*Åbo*

Akademi University). Dr Werkelin also directly contributed to this thesis with the Swedish translation of the abstract. Tack Johan!

It would not have been possible to complete this thesis without the help of numerous people working at Åbo Akademi Process Chemistry Centre Laboratory of Inorganic Chemistry during the years 2007–2011 who though not mentioned are not forgotten. I appreciate your help whenever I needed assistance. I thank you not only for always having open doors, but also for your readiness to engage in scientific discussion and to help with all kinds of experimental and organizational aspects. I thank you too for your friendship. I want to express my special thanks to Peter Backman, Luis Bezerra, Tor Laurén, Piia Leppäsalo, Jaana Paananen, and Linus Silvander for their continuous assistance with different aspects of the experimental world.

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To my mother and my sister, the distance has been painful, since you mean everything to me.

"Without creative personalities able to think and judge independently, the upward development of society is as unthinkable as the development of the individual personality without the nourishing soil of the community."

Albert Einstein

Åbo, February 2012

Patrycja Piotrowska

Abstract

The currently-used sources of biomass are limited so new ones are required in order to meet the European Union target and to satisfy the constantly-increasing demand for energy. This is why energy recovery from residues or waste derived fuels has been given considerable attention over recent years.

The residues generated during the production of biofuels for transportation are often the main stream from the production plant. Proper allocation of the residues could significantly improve the sustainability of the production process resulting in high greenhouse gas emission savings and improvement in their profitability. Energy recovery could be one application, among others, for the residues.

The objective of this study was to investigate the combustion behaviour of four residues from the production of biofuels for transportation. The residues of interest were: rapeseed cake, palm kernel cake, dried distillers' grains with solubles, and fermented sewage sludge. A wide range of methods of laboratory to semi-industrial scale was applied in order to define the main challenges related to the fluidized bed combustion of these residues.

All residues were characterized by means of laboratory methods. The residues differ substantially in their composition compared to more traditional biomass fuels. Their common property is a high concentration of phosphorus. Until recently, phosphorus was considered a negligible element for ash chemistry due to its low concentrations.

Rapeseed cake was further studied, as an example of phosphorus-rich fuel, during bench-scale bubbling fluidized bed (BFB) and semi-industrial scale circulating fluidized bed (CFB) combustion experiments. Rapeseed cake, with phosphorus and alkali metals dominating its ash chemistry, led to defluidization at approximately 800 °C. Bed sintering during fluidized bed combustion of pure rapeseed cake followed a non-reactive mechanism. This mechanism is controlled by the stickiness of fuel-derived ash particles. Entrained fine rapeseed cake ash particles also aggravated deposit formation. In order to improve the

problematic behaviour two strategies were used: co-combustion and the use of limestone. Three different base fuels were used: bark, wood, and coal.

Co-firing of rapeseed cake with a minimum of 60 wt% of bark in a bench-scale BFB reactor increased the defluidization temperatures compared to the pure rapeseed cake case. This was correlated with the increase of the Ca/P molar, which increased with a higher proportion of bark in the fuel mixture. During co-firing with wood in a semi-industrial scale CFB combustor, the addition of limestone was found to be necessary in order to improve the bed sintering tendency of the fuel mixture.

Co-firing of rapeseed cake with coal in a semi-industrial CFB combustor did not show any significant operational problems. Therefore co-combustion with coal is considered to be one of the strategies to improve combustion of phosphorus-rich biomass.

The experimental work in this study revealed that phosphorus has a role during combustion which cannot be neglected when phosphorus-rich fuels are entering the energy market. Challenges during fluidized bed combustion of the residues were defined and countermeasures were investigated.

Sammanfattning

Tillgången på traditionella biobränslen är begränsad och därför behöver nya biobränslen tas fram för att möta de uppställda målen av EU och det ständigt ökande energibehovet. Under de senare åren har intresset riktats mot energiutvinning ur restfraktioner och avfall.

Vid produktionen av fordonsbränsle ur biomassa är den fasta restprodukten ofta den största processströmmen i produktionsanläggningen. En riktig hantering av restprodukterna skulle göra produktionen mera lönsam och mer ekologiskt hållbar genom att t.ex. minska utsläppen av växthusgaser. Ett alternativ är att utvinna energi ur dem.

Målsättningen med den här avhandlingen är att studera förbränningsegenskaperna hos några fasta restprodukter som uppstår vid framställning av förnybara fordonsbränslen. De fyra undersökta materialen är rapskaka, palmkärnskaka, torkad drank och stabiliserat rötslam. I studien används ett stort urval av undersökningsmetoder, från laboratorieskala till fullskalig förbränning, för att identifiera de huvudsakliga utmaningarna förknippade med förbränning av restprodukterna i pannor med fluidiserad bäddteknik.

Restprodukterna undersöktes med metoderna i laboratorieskala. De skiljer sig alla från traditionella biobränslen genom att ha en annan kemisk sammansättning än dessa. Vanligtvis har de betydligt högre halter av fosfor. Tidigare har man inte uppmärksammat fosforns roll i biobränsleaskans högtemperaturkemi eftersom halterna ansetts vara så låga.

Rapskaka är ett potentiellt biobränsle men med mycket hög fosforhalt. Då den brändes i en fluidbäddreaktor av typ bubblande bädd i liten bänkskala sintrade sandbädden redan vid 800 °C på grund av fosfordominerad askkemi i kombination med alkalimetaller. Bäddsintringen vid förbränning av rapskakor i fluidbäddsförbränning följde en icke-reaktiv mekanism som kännetecknas av att sintringen orsakas av klibbiga askpartiklar från bränslet. Askan som lämnar bädden med rökgasen orsakar även beläggningsbildning högre upp i pannan. För att komma till rätta med problemet testades två strategier:

sameldning med andra bränslen samt tillsats av kalksten. Tre olika bränslen sameldades med rapskakan: bark, trä och stenkol.

Vid sameldning i bänkskala med 60 viktsprocent bark kunde sintringtemperaturen höjas jämfört med fallet med endast rapskaka som bränsle. Högre andelar bark i bränslemixen höjer molförhållandet Ca/P. Vid sameldning med ved i en fullskalig fluidbäddpanna av typ cirkulerande bädd måste även kalksten tillsättas för att minska benägenheten hos sandbädden att sintra. Vid sameldning med kol i samma fullskalepanna kunde förbränningen fortgå utan några problem. Slutsatsen var att sameldning med kol är ett av huvudalternativen för att förbättra förbränningen av biomassor med höga fosforhalter.

De experimentella undersökningarna i den här studien visar att fosfor har en betydande roll som inte kan förbises då biomassor med hög fosforhalt kommer in på biobränslemarknaden. I avhandlingen definieras utmaningarna vid förbränning av restprodukterna i fluidbäddpannor och förslag undersöks till möjliga åtgärder.

Table of contents

List of publications in this thesis

I. Giuntoli J., de Jong W., Verkooijen A. H. M., **Piotrowska P.,** Zevenhoven M., Hupa M. Combustion Characteristics of Biomass Residues and Biowastes: Fate of Fuel Nitrogen. Energy & Fuels 2010, 24, 5309–5319.

II. **Piotrowska P.,** Zevenhoven M., Hupa M., Giuntoli J., de Jong W. Residues from liquid and gaseous biofuels production–fuel characterization and ash sintering tendency. Fuel Processing Technology 2011, doi: 10.1016/j.fuproc.2011.09.020.

III. **Piotrowska P.,** Grimm A., Skoglund N., Boman C., Öhman M., Zevenhoven M., Boström D. and Hupa M. Fluidized bed combustion of mixtures of rapeseed cake and bark: the resulting bed agglomeration characteristics. Energy & Fuels 2012, doi: 10.1021/ef300130e.

IV. **Piotrowska P.,** Skoglund N., Grimm A., Boman C., Öhman M., Zevenhoven M., Boström D. and Hupa M. Systematic studies of ash composition during co-combustion of rapeseed cake and bark. Accepted for the proceedings of the 21st International Conference on Fluidized Bed Combustion, Naples (Italy), June 2012.

V. **Piotrowska P.,** Zevenhoven M., Davidsson K., Hupa M., Åmand Lars-E., Barišić V., Coda Zabetta E. Fate of alkali metals and phosphorus of rapeseed cake in circulating fluidized bed boiler part 1: co-combustion with wood. Energy & Fuels 2010, 24, 333–345.

VI. **Piotrowska P.,** Zevenhoven M., Davidsson K., Hupa M., Åmand Lars-E., Barišić V., Coda Zabetta E. Fate of alkali metals and phosphorus of rapeseed cake in circulating fluidized bed boiler part 2: co-combustion with coal. Energy & Fuels 2010, 24, 4193–4205.

Contribution of the author

Paper I   The author was taking part in the planning stage of the combustion tests. She was responsible for 40% of experiments and their evaluation. Giuntoli was the main author of the paper.

Paper II   The author was responsible for planning of the experiments. She did the experimental work and the evaluation of the results. She was the main author of the paper.

Paper III   The author was responsible for planning of the experiments. She did the experimental work together with co-authors. She was responsible for the evaluation of the results and was the main author of the paper.

Paper IV   The author was responsible for planning of the experiments. She did the experimental work together with co-authors. She was responsible for the evaluation of the results and was the main author of the paper.

Paper V   The author did the laboratory scale experiments. She was responsible for the evaluation of the results and was the main author of the paper.

Paper VI   The author did the laboratory scale experiments. She was responsible for the evaluation of the results and was the main author of the paper.

Other publications produced related to this thesis

I.   **Piotrowska P.**, Zevenhoven M., Hupa M., Davidsson K., Åmand L.E., Coda Zabetta E., Barišić V. Fate of phosphorus during co-combustion of solid biofuels. The 20th International Conference on Fluidized Bed Combustion, Xi'an City (China), May 2009 (*peer-reviewed conference article and oral presentation*). Extended results and rewritten version published as Paper V.

II. **Derda P.**, Zevenhoven M., Hupa M., Davidsson K., Åmand L.E., Kassman H., Coda Zabetta E.; Fate of alkali metals during co-combustion of biodiesel residues with coal in a semi-industrial CFB boiler. The 9th International Conference on Circulating Fluidized Beds, Hamburg (Germany), May 2008 (*peer-reviewed conference article and oral presentation*). Extended results and rewritten version published as Paper VI.

III. **Piotrowska P.**, Zevenhoven M., Hupa M., Giuntoli J., de Jong W. Residues from liquid and gaseous biofuels production–fuel characterization and ash sintering tendency. Impacts of Fuel Quality on Power Production & Environment, Lapland (Finland), August 2010 (*conference article and poster*). Rewritten and published as Paper II.

IV. **Piotrowska P.**, Grimm A., Skoglund N., Boman C., Öhman M., Zevenhoven M., Boström D. and Hupa M. Systematic studies on defluidization temperatures of rapeseed cake and bark mixtures. Scandinavian-Nordic Section of Combustion Institute Meeting 2011, Trondheim (Norway), November 2011 *(Extended abstract and oral presentation)*.

V.   Zevenhoven M., **Piotrowska P.**, Giuntoli J., Hupa M. Fuel characterization at Åbo Akademi–an update. The International Energy Agency–Fluidized Bed Conversion (IEA-FBC) meeting, Częstochowa (Poland), October 2009 *(Oral presentation given by M. Zevenhoven)*.

VI. **Piotrowska P.**, Zevenhoven M., Hupa M., Barišić V., Coda Zabetta E. Analysis of bed material from co-combustion of biomass fuels in CFBC. Scandinavian-Nordic Section of Combustion Institute Topical Meeting 2008 on Measuring Techniques in Combustion, Gothenburg (Sweden), October 2008 *(Extended abstract and oral presentation)*.

1 INTRODUCTION

1.1 Context

1.1.1 The European energy market

One of the key targets set by the European Council to be reached by 2020 is to increase the renewable energy share to 20% in European Union energy consumption.[1] This energy share corresponds to approximately 4.2 PWh based on the total primary energy consumption in 2008.[2] In order to meet this target, still more effort is needed since the share of renewables in energy consumption was at the level of only 8% in 2008.[3] Currently the main renewable source of energy is biomass (Figure 1) and the overall tendency in the energy sector has been to use biomass, thereby partially replacing the use of fossil fuels. The present sources of biomass are limited and new ones are required in order to meet the European Union target and to compensate for the constantly increasing energy demand. Therefore energy recovery from residues or waste derived fuels has been given greater attention over the past years.

The production of liquid and gaseous biofuels for transportation and residues from the processes has become a source of biomass residues that can be used in the energy sector.
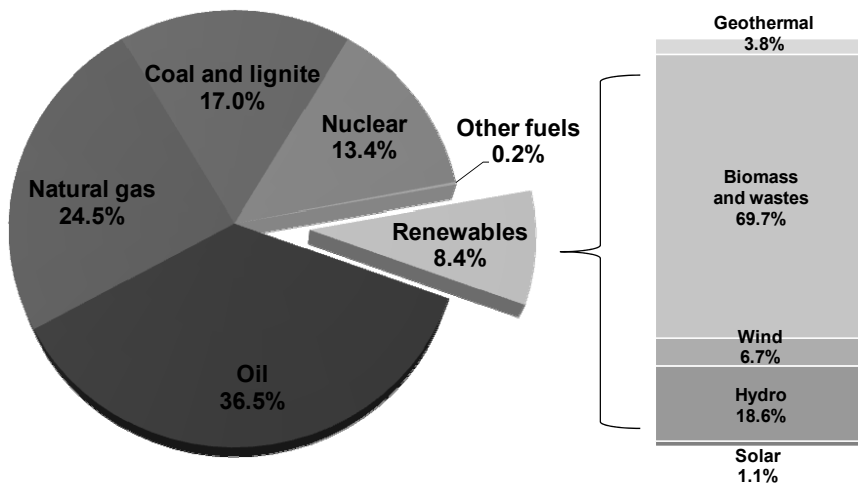
Figure 1 *Total primary energy consumption in 2008 (EU-27) [3].*

The transportation sector is constantly growing and some liquid and gaseous biofuels are already implemented (Figure 2)[4], while R&D works on more advanced processes[5]. The advantages and disadvantages for the production of biofuels in the transportation sector are continuously discussed.[6-11] The largest concerns are related to an increase in food prices, land use and

Figure 2 *EU targets and share of biofuels in road transport consumption (EU-27) based on EEA – Eurostat, data for 2009 from [4].*

biodiversity, and the overall environmental impact. Opinion is here divided. The common attitude is that the production should be sustainable and cost-effective. The evaluation of the sustainability of the first generation biofuels may be often overrated. Taheripour et al.[12] argue that studies reporting on the impacts of their production often do not take the use of the residues into consideration. The use of the residues could mitigate the price impacts, demands for cropland and the indirect land use consequences of first generation biofuels.

1.1.2   Biofuels for transportation

The main biofuel produced globally is bioethanol[13], but biodiesel is the main biofuel produced in EU−27 (Figure *3*). Biogas is used to generate electricity and heat rather than as a transportation biofuel.[14-15] However, its consumption as transportation fuel is increasing. An increase of 40.1% yearly is observed and is almost unique to Sweden while other countries are in the developmental stage.[14]
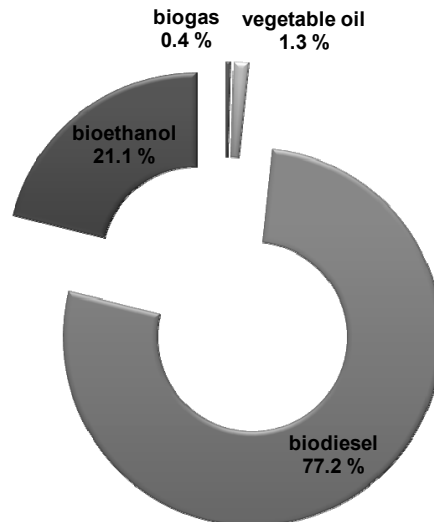
Figure 3 *Total biofuel consumption for transport by biofuel type in EU-27. Estimation for 2010 based on EurObserv'ER 2011 [14].*

Bioethanol, a substitute for gasoline, can be produced from different feedstocks (Figure 4) which serve as a source of sugar for fermentation processes. The production process consists of three main stages: hydrolysis, fermentation, and distillation.[16-19] The main residue of the distillation process is stillage, called distillers grains and solubles (DGS). It can be sold as a protein-rich animal feed. Due to its high water content (88% ar) it is further dried in order to extend its shelf life.[17] The name of the dried product is dried distillers' grains with solubles (DDGS). Its water content is approximately 9% on a received basis.[17] Thermal conversion is an alternative use of the residues. Application of DGS or DDGS in the ethanol mills could be beneficial in both economic and environmental terms.[20-21] For this purpose the moisture content should be lower than 70% on a received basis in order to achieve a good level of heat and power efficiency.[20]

Biodiesel, a substitude for fossil diesel, is the most common biofuel produced in Europe. Currently, Germany, France, Italy, and Spain dominate the European
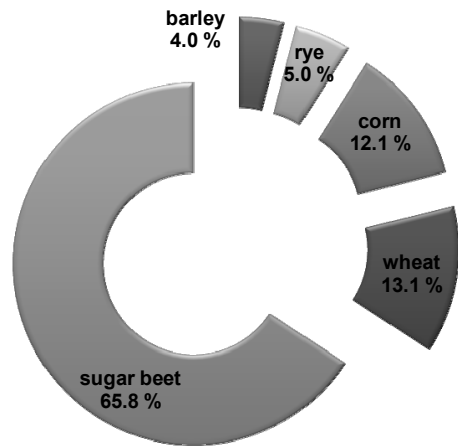
Figure 4 *Feedstock used for bioethanol production in EU-27 in 2009 based on EU FAS posts reported in USDA Annual Biofuel Report 2011 [15].*
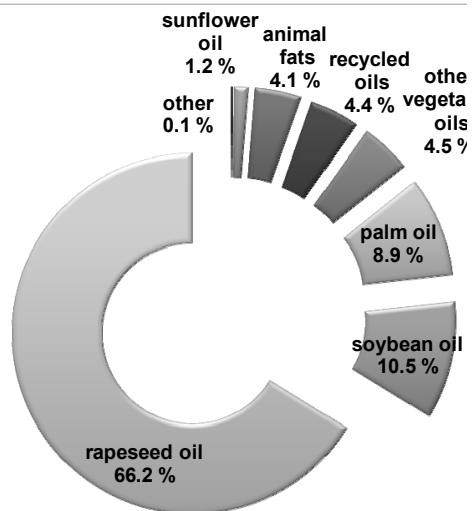
Figure 5 *Feedstock used for biodiesel production in EU-27 in 2009 based on EU FAS posts reported in USDA Annual Biofuel Report 2011 [15].*

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biodiesel market, with Germany contributing to nearly half of the overall production.[9,16,22] Fatty acid methyl ester (FAME), commonly called biodiesel, is considered to be a first–generation biofuel. It can be produced from various components, e.g., vegetable oil, animal fats, waste oils and fats. However, oilseed plants are the main feedstock (Figure 5). Pressing or solvent extraction of straight vegetable oil (SVO) is an intermediate step in the process. Triglycerides are further upgraded into alkyl–fatty esters via transesterification.[16] Two residues from biodiesel production were studied in the present work: residue from rapeseed methyl ester (RME) and from palm oil methyl ester (PME) production. RME, derived from rapeseed oil, is the most common biodiesel fuel available in Europe with press cake (rapeseed cake) or extraction meal (rapeseed meal) the main residue.[15] Palm oil is the third most common feedstock for the biodiesel production in EU-27 (Figure 5).[23] The residue from the pressing of palm kernels is the palm kernel cake.

Biogas consists mainly of methane and carbon dioxide.[24-25] However, the composition of biogas can vary.[26] It can be produced from all kinds of biomass.[24-25] Three main production sources of biogas are shown in Figure 6. Half of European biogas is produced at landfill and wastewater treatment plants. Other sources of biogas are among others, energy crops and municipal solid wastes.[27] Biogas production is considered to be the best environmental waste energy recovery and its use is increasing from year to year.[27,28] Germany and the United Kingdom are the main producers of biogas in EU-27 (Figure 7). Biogas is used at units designed for natural gas or liquefied petroleum gas (LPG).[29] The most common way of biogas utilization is in combined heat and power (CHP).[24,25] The
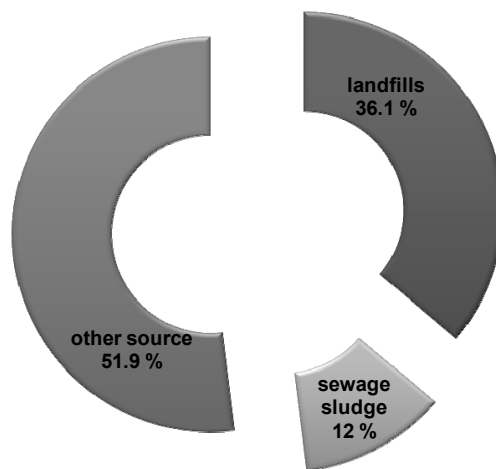
Figure 6 *Primary biogas output in the European Union in 2008 by biogas source based on total output (ktoe). Data source EurObserv'ER 2010 via [27].*

use of upgraded biogas in the transport sector is gaining increased attention, especially in Sweden and Switzerland.[28] Depending on the applications, biogas needs to fulfil different requirements related to fuel quality. Rasi et al.[26] indicate that if biogas is to be considered as a vehicle fuel, it is advised to produce it from manure or sewage sludge since these biogases are the easiest to upgrade. The residue from biogas production can be called fermented sewage sludge.
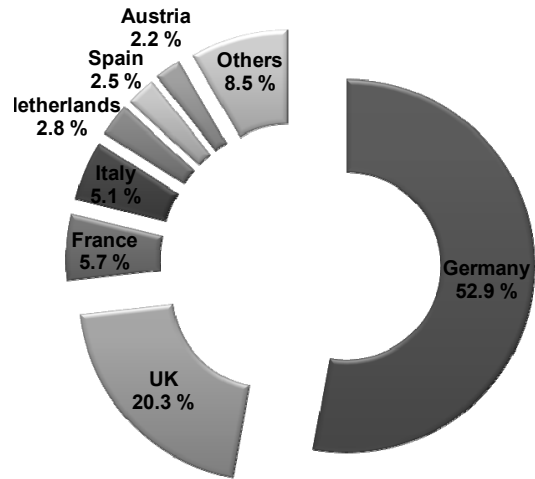
Figure 7 *Primary biogas output in the European Union in 2008 by country based on total output (ktoe). Data source EurObserv'ER 2010 via [27].*

1.1.3   The use of the residues from the production of biofuels for transportation

The residues generated during the production of biofuels for transportation are often the main stream from the production plant.[19,30] Proper allocation of the residues could significantly improve the sustainability of the production of biofuels resulting in high greenhouse gas emission savings[31-33] and also improve their profitability[19,20,30]. Some of these residues are rich in proteins and could be used in varying quantities as animal feed.[34] However, before deciding on the feed intake rates, the nutritional and antinutritional properties of feed, its digestibility, and the protein and nitrogen balance need to be taken into account. Feed properties need to be known beforehand in order to avoid detrimental effects to animal health and performance.[35-39] Low intake rates, e.g. 10-15% of total feed for rapeseed cake with low levels of glucosinolates[40,41], and increased production of the residues can lead to a saturation of the market. Energy recovery could be an alternative application for the residues. In some cases, the use of the residues in combined heat and power plants is reported to be the most favourable usage, improving sustainability of biofuels production.[20,21,32]

1.2 Objective

It can be observed that a substantial part of our economy is based on biomass. However, biomass resources are limited and therefore the optimal allocation of biomass resources over different applications is the main challenge. The motivation of this work comes from the understanding that all viable routes need to be well understood before determination of the final use. The application of main interest in this thesis is energy recovery.

The objective of this study was to investigate the fluidized bed combustion behaviour of four residues from the production of biofuels for transportation. The residues of interest were: fermented sewage sludge (FSS) from biogas production via anaerobic fermentation, dried distillers' grains with solubles (DDGS) from barley bioethanol production, rapeseed cake (RC) and palm kernel cake (PKC) – the residues from oil extraction. A wide range of methods from laboratory to semi-industrial scale was applied in order to define challenges related to the combustion of the residues. The main focus was to establish the role of phosphorus in the combustion process especially bed sintering. The final goal was to pave the way for more extensive use of these residues in heat and power production using fluidized bed technology.

1.3 Summary of publications

Within the frame of this work laboratory, bench-scale, and semi-industrial scale experiments were performed and the results are presented in six journal publications.

The four residues were investigated in a laboratory scale to determine their combustion properties and challenges that could occur during combustion. Results are presented in *Papers I and II*. High concentration of phosphorus in the fuel has an influence on sintering behaviour. Consequently, rapeseed cake, as an example of phosphorus-rich fuel, was further studied in fluidized bed combustion conditions in a bench-scale (*Papers III and IV*) and semi-industrial scale (*Papers V and VI*).

The combustion properties shown in *Paper I* were studied in a co-operation with Delft University of Technology. Laboratory scale experiments were performed in a single

particle reactor. This study showed that the residues have a good combustion potential. The focus was on the release of gaseous compounds during different stages of combustion. Ash-forming matter was studied in *Paper II*. Fuel properties were related to the ash sintering tendency (Figure 8). In all four

Figure 8 *Summary of paper II.*

fuels a high concentration of phosphorus was found involved in the sintering behaviour.

In *Paper III* systematic studies in a 5 kW bench-scale bubbling fluidized bed reactor are described. The studies were performed in order to evaluate the risk of agglomeration in a fluidized bed boiler during co-combustion of rapeseed cake with spruce bark, a calcium rich biomass. Tests were carried out during an exchange visit at Umeå University as part of a joint collaboration with Luleå University of Technology. The studies show that bark (high in calcium) improves the combustion of rapeseed cake. In *Paper IV* the same experiments were taken into consideration. In this study a detailed investigation of particles in bottom and fly ash has been performed by means of SEM/EDX analyses. The aim of the study was to determine ash composition resulting from the combustion of rapeseed cake-bark fuel mixtures.

Paper V and *Paper VI* show results from the semi-industrial scale combustion of rapeseed cake. The main focus of the study was ash behaviour during co-combustion of rapeseed cake with wood and coal as base fuels. The influence of addition of limestone was also investigated. The measurement campaigns were carried out at Chalmers University of Technology. *Paper V* shows that limestone addition decreased the agglomeration risk while *Paper VI* shows that co-combustion with coal can be another strategy to improve the combustion of rapeseed cake. Interesting synergies between the ashes and additives have been observed in both papers.

2 BACKGROUND

2.1 Fuel Characterization

Appropriate fuel characterisation is of great importance in respect to industrial application. Fuel properties and the manner in which those properties influence the outcome of the combustion process are necessary for the process design and control.[42,43] The aim of fuel characterization is therefore to determine the main challenges and benefits of fuel application. There are many laboratory and bench-scale methods that are applied for fuel characterization. All of them could be

Figure 9 *Areas of fuel characterization research.*

grouped into five main research areas (Figure 9), which often overlap with one another.

Fuel physical properties, like bulk density, particle size or pellet durability, together with moisture content, are important properties for fuel handling. Within this group the heat content is also useful information when planning storage[44], and it defines the feeding rate.

A first indication of combustion behaviour, availability, and emissions can be made based on standard fuel analysis. Standard fuel analysis is a standardized group of analytical methods comprising proximate analysis, ultimate analysis, and elemental analysis. The analyses are commonly used and thoroughly described.[42,43,45-48] Their short description is given below.

Proximate analysis distinguishes moisture, volatile matter, fixed carbon, and ash in a fuel sample. It serves as the combustion behaviour indicator. It is based on the main combustion stages of a fuel particle as shown in Figure 10. When a fuel particle is introduced to a combustion atmosphere, at first it dries and then there is a release of
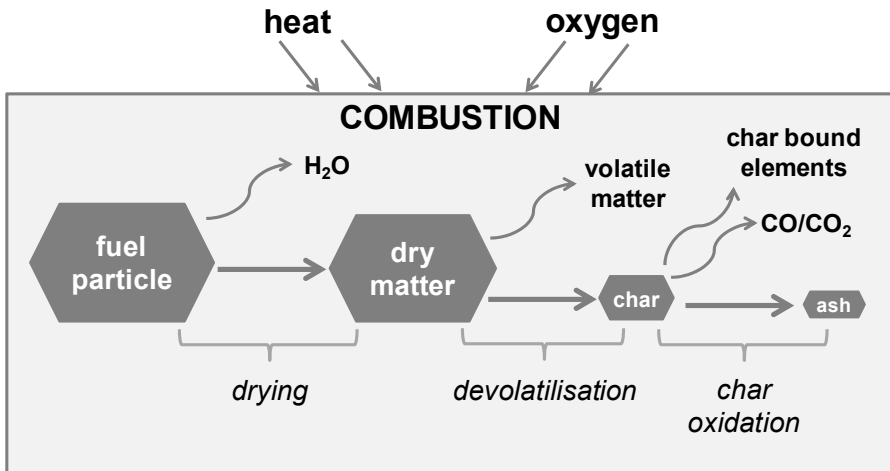
Figure 10 Combustion stages.

volatile matter: this is called the devolatilization stage. The released volatile matter undergoes homogeneous oxidation, whereas the remaining char undergoes heterogeneous oxidation. The solid residue after combustion is ash.

The ultimate analysis, giving a first estimation of emissions, determines carbon, hydrogen, nitrogen, sulphur, and chlorine, with oxygen usually calculated as the difference between 100 and the sum of the percentage content of the other elements. Large variations between biomass fuels were summarized by Vassilev et al.[49]. The difference in moisture content and ash yields can bias the results of the analysis. Therefore it is better to use results on a dry or dry ash free basis for comparative characterisation.[49]

Elemental analysis includes the analysis of ash-forming elements for the prediction of the ash composition. It is important to know the composition of ash since it can cause a decrease of combustor availability. The elemental analysis results are usually reported in terms of the most common oxides (wt% of ash), indicating that the analyses were performed on an ashed fuel sample.[50] Elemental analysis could also serve as the indicator of potential ash utilization. The use of ash as a fertilizer is one of the options. Recirculation of nutrients by spreading the ashes from heat and power plants could prevent nutrient export due to harvesting.[51] Of special importance in this respect are heavy metals[42], the presence of which could limit or even prohibit fertilisation with ash.

The standard fuel analysis can be used as a starting point in establishing the suitability of the fuel for combustion units, but it is not enough for designing and controlling the combustion process. Both fuel properties and process conditions, such as the temperature or excess air ratio, are crucial for determining combustion behaviour, combustor availability, and emissions.[48] Therefore fuels are studied at specific conditions and often in test rigs of different scale, e.g., laboratory-, bench- or full-scale in order to provide vital information on chemical, physical, and kinetic properties.

2.2   *Combustion properties of biomass fuels*

Biomass is an issue with a relatively long history but which still requires detailed studies in order to solve challenging problems. The combustion behaviour differs greatly compared to fossil fuels[52], which is a result of its different composition[49]. Combustion of biomass, and related operational problems, has been extensively reported in the literature.[43,44,47,48] Ash chemistry is of significant importance in the field of fuel characterization since it defines the suitability for combustion technology.

Conversion in fluidized bed is the preferable technology for combustion of fuels with varying quality like some biomass and wastes or fuel mixtures.[47,48,53-55] Since it is flexible, it produces low emissions and has a high level of efficiency. The main challenges, as reported, are related to ash chemistry.[48,52,55-60] The main ash-related problems discussed in literature[56] are: agglomeration (sintering of fluidized bed)[61-63], fouling (heat exchanger tube deposit)[57,64-67], high temperature corrosion[64,68-73], and slagging (furnace deposit)[60,74-76]. Determination of ash properties is crucial to avoid these problems and consequent costs. Ash properties differ from fuel to fuel and therefore the analyses should be performed on a case-by-case basis.

For many biomass fuels, alkali metals (K and Na) and chlorine are usually considered the main ash constituents responsible for the ash-related problems. Many studies related to different aspects of alkali metals can be found in literature.[77-79] The reason is that, together with sulphur, they are the main factors lowering the first melting temperature of ash.[43,52] During biomass combustion, potassium ends up in the ash in the form of chloride (KCl),

sulphate (K_2SO_4), carbonate (K_2CO_3), and hydroxide (KOH).[80,81] Sodium in combustion is generally following the fate of potassium. All these compounds have rather low melting temperatures, and some of them are even volatile at normal combustion temperatures (700-1000 °C).[82] A good understanding of the chemistry was gained and prevention methods were suggested.[70,73,81,83,84]

However, recent studies have shown that a high content of phosphorus in a fuel can have a crucial impact on combustion behaviour as well.[85-87] being responsible for the formation of low melting temperature ash.[88] The role of phosphorus has been neglected until recently due to its low concentrations in many biomass fuels. It is a newly recognized property in some biomass.

2.3   Bed sintering in fluidized bed combustion of biomass fuels

Agglomeration or bed sintering during (co-)combustion of biomass fuels has been studied by several research groups.[55,62,83,87,89-101] Both terms, agglomeration and bed sintering, are used alternatively to describe the same phenomenon. Sintering may be defined as the formation of bonds between particles at high temperatures[102], while agglomeration may be defined as the formation of clusters of particles, so called agglomerates. The agglomeration of bed material in a fluidized bed reactor at elevated temperatures can thus be defined as the sintering of bed material. The tendency of the bed particles to agglomerate can cause defluidization and so limit the operation of fluidized beds.[89]

The mechanisms of sintering have been extensively studied in the field of material science, since most bulk ceramic components and glass are made by sintering of compressed powder.[102] The same mechanisms of sintering could be used to describe sintering of ashes and bed material in fluidized bed combustors. Skrifvars et al.[103] defined three different mechanisms responsible for sintering of ash in fluidized beds: partial melting, partial melting with a viscous liquid (or viscous flow sintering), and gas-solid chemical reaction.

Partial melting refers to sintering through the appearance in fuel-derived ash particles of a liquid phase consisting of molten salts. The amount of melt controls the ash stickiness and is considered to be the controlling parameter for agglomerate formation. Partially molten ash can lead to bed sintering. This phenomenon is described in literature as "melt induced agglomeration"[104], or direct adhesion of bed material grains by molten particles[105]. The influence of char burn-out on the formation of molten phases was studied by Lin et al.[62] and Scala et al.[100,106]. They suggested that the temperature of burning char particles could be higher than that of the average bed temperature, resulting in melt formation. The difference between the burning particle temperature and the bed temperature may be in the range of 40-600 K (in[107] based on[108]).

Partial melting with viscous flow is another sintering mechanism referring mainly to silicate systems. Silicon can form highly polymerized silicate networks for which the liquid phase formed at temperatures above the solidus temperature may be highly viscous. The molten phase of simple salts shows low viscosity. The formation of a highly viscous liquid could occur for the fuel ash particles (as in coal combustion in pf-boilers) and bed material containing silicon. While the first one describes the formation of highly viscous melt originating from the fuel-derived ash, the second points to the interactions of the released inorganic compounds with the bed material, leading to the formation of a layer on the bed grains. Depending on the composition, the layer could be sticky and a prerequisite for the formation of agglomerates.[92,97] In this case the initial composition of the layer is an important parameter for bed sintering, depending on both the fuel-ash composition and ash-bed material interaction processes.[104]

The third sintering mechanism mentioned by Skrifvars et al.[103] is gas-solid interaction (or chemical reaction sintering). These were reported only in respect to the deposit formation in the convective pass of the boiler. However, the chemical reaction of gaseous species, e.g. alkali metals, with the bed material, has been also shown to occur in fluidized beds during biomass combustion. The layers on grain surfaces have been found[83,95,96,104] and divided according to their composition. The layer rich in potassium is referred to as inner

reaction layer.[87,109] Potassium silicates can have a first melting temperature as low as 750 °C[97] and their formation can lead to viscous flow bed sintering.

A different perspective on the formation of agglomerates is shown by De Geyter[110] and Visser et al.[104]. They described bed sintering with respect to interactions between bed material grains and fuel-derived ash, distinguishing two cases. One is case when a chemical reaction between bed

Figure 11 *Summary of bed sintering mechanisms.*

material particles and ash is taking place, which could be referred to as a reactive mechanism, and the other when no chemical reaction between the bed material particles and ash takes place. The latter could be then called a non-reactive mechanism. The summary of bed sintering mechanisms is shown in Figure 11.

All research groups point to the significant role of alkali metals in the formation of agglomerates.[83,92,97] However, recent studies also indicate phosphorus as the element aggravating bed agglomeration.[75]

2.4 Phosphorus in biomass and its chemistry during combustion

Phosphorus is an essential element for plant growth and plays a role in an array of processes including nucleic acid synthesis, photosynthesis, nitrogen fixation etc.[111,112]. Therefore it is necessary for the development of new cells and seed formation, making it one of the elements limiting the crop yield.

As reported by Marschner[113], in the early stages of seedling growth the embryo has a large requirement for mineral nutrients, including magnesium, potassium, and phosphorus. In seeds and in grains, phosphorus is typically stored in the form of phytic acid, myoinositol, 1, 2, 3, 4, 5, 6-hexakiphosphate[114,115] (Figure 12) and its salts, phytates. Phytate phosphorus

makes up 50% of the total phosphorus in legume seeds, 60-70% in cereal grains, and about 86% in wheat mill bran. In legume seeds and cereal grains the main phytates are magnesium-potassium salts. The proportions of potassium, magnesium, and also of calcium associated with phytic acid might considerably vary between plant species and even between different tissues of a seed.[113]
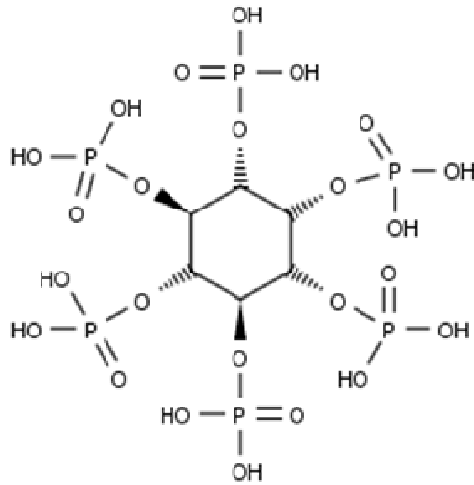
Figure 12 *Phytic acid structure according to [123].*

Due to its low concentrations in biomass, to date, its role during combustion has been considered negligible even though some studies on phosphorus were performed.[116] This macro nutrient is present in substantial amounts in some biomass fuels. It is mainly present in high concentrations in agricultural biomass and animal wastes (chicken litter, meat-bone-meal) and sewage sludge.[49] A high concentration in fuel increases its content in formed ash. However, the ash properties are different depending on the fuel origin. Fly ash from meat-bone-meal consists mainly of apatite[117], and in sewage sludge ash calcium magnesium phosphate and aluminium phosphates were found.[118] The found phosphates have high melting temperatures. Thus no ash sintering should occur at fluidized bed combustion temperatures. For agricultural biomass, however, formation of low melting temperature phosphates is reported.[85,119] Bäfver et al.[120] found potassium and phosphorus dominating the fine fly ash particle fraction (<1 µm) and the molar ratio indicating the formation of KPO_3 and KH_2PO_4 during combustion of second-rate oat grains. These compounds can have a significant influence on deposit formation and agglomeration.

The combustion behaviour of fuels rich in phosphorus is different compared to woody fuels.[75,85,87,121] In woody biomass a negligible amount of phosphates is formed. Alkali metals

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are available for the reaction with bed material or silicon present in the fuel. Since phosphorus dominates over silicon in the competition for the base cations: K^+, Mg^{2+}, Ca^{2+}; phosphates will form preferentially to silicates during combustion of P-rich fuels.[119] This K-capturing ability of phosphorus was also observed during fluidized bed combustion of phosphorus-rich biomass.[87,121] It was concluded that the formation of phosphates prevented the formation of the inner reaction layer. The reason was that the reduced amount of potassium was available for the reaction with quartz bed material grains. If the formed phosphates show a high K/Ca

Figure 13 *$CaO–K_2O–P_2O_5$ diagram (on molar basis), showing melting behaviour of some available compounds. Diagram according to [125] based on [123].*

ratio, however, ash of low melting/sintering temperature range could form.[86] Partly molten ash particles containing K-Mg-P and Ca-K-Mg-P were reported to adhere to the bed material grains during fluidized bed combustion[87], leading to bed agglomeration. Therefore it seems that phosphorus in regard to ash-related problems seems to show a dual behaviour depending on the concentration of alkaline earth metals in the fuel/ash (Figure *13*).

Phosphorus in ash occurs as orthophosphates (PO_4^{3-}), but it can also occur in other structures like polymeric ions such as metaphosphates ($P_3O_9^{3-}$) and pyrophosphates ($P_2O_7^{4-}$) as summarized by Lindberg et al.[88]. The formation of tripolyphosphates ($P_3O_{10}^{5-}$) in biomass ash samples was also reported by Boström et al.[121]. Lindberg et al.[88], based on[122], concluded that orthophosphates have the highest melting temperatures. This finding is supported by melting temperatures shown in Figure 13 (based on[123]). Therefore the formation of orthophosphates in ash is desirable during the combustion of phosphorus-

rich fuels. In fluidized bed combustion, phosphate-dominated ash is present in the bed material which is often silica based. Silicon also enters the combustion chamber with fed fuel. The reaction of phosphates with silicates at the fluidized bed temperatures is suggested.[75,86,121] Lindberg et al.[88] stated that phosphates are miscible with silicate liquids and may lower the melting temperatures of silicate-rich ashes.

The influence of MgO and/or CaO on the increase of melting point of phosphates was reported by Lindström et al.[85] and further experimentally studied by: Barišić et al.[75], Steenari et al.[86], Boström et al.[119], and Hao et al.[124]. In these studies limestone was used as a calcium source. Studies on laboratory-prepared ash samples[86] showed that with additives the potassium-rich phosphate phases incorporate calcium and also magnesium to form phosphates with a higher Ca(Mg)/K molar ratio, so the melting point becomes higher. The other studies show results from bench- and full-scale combustion experiments in both fluidized and grate firing technology. Phosphorus was captured to a higher degree in the bottom ash during limestone addition compared to the combustion of pure oats, though the formation of slag increased.[119] The formation of potassium phosphates in the fly ash fraction of ash was reduced with limestone addition.[119,120] Limestone is expected to favour the formation of phosphates with a high melting temperature but it has an additional role in fluidized beds, where it was observed to coat silica particles, thereby preventing the formation of low melting temperature silicates.[75]

In order to better understand the use of Ca/P-based additives to reduce ash-related problems, Novaković et al.[125] investigated the release of potassium from laboratory prepared salt mixtures in Ca-K-P system. They found that the Ca/P molar ratio has an influence on the release of potassium from the system if potassium carbonate is used as a potassium source. They concluded that potassium in this case is incorporated in non-volatile phosphate structures. However no influence of Ca/P ratio on potassium release was observed when KCl was used as a potassium source. The release of KCl from the sample was observed after 90 min of each performed experiment. During combustion of phosphorus-rich fuel, an increased formation of KCl was observed when limestone was added in a small-scale combustion[119], and it was observed that Ca-based additive

promoted vaporization of potassium with no significant effect on the release of phosphorus in a tube reactor[124].

Additionally in some works also the influence of kaolin on the ash behaviour was studied.[86,119,120] The combustion of phosphorus-rich fuels was improved, meaning that ash-related problems minimized. Based on laboratory studies the best antislagging effect is expected when both additives are used.[86]

The behaviour of a phosphorus-rich fuel can differ depending on the combustion conditions and other ash-forming elements present in the fuel. Even though some understanding of phosphorus chemistry has been gained, there is still much to be known.

2.5   Thermal conversion of the residues

2.5.1   Dried distillers' grains with solubles

Thermal conversion of DDGS was studied by several authors.[126-132] The literature on combustion properties and ash-related problems is scarce, however. It has been stated that DDGS is a promising feedstock for char production.[129] Gasification of DDGS results in considerable H_2 and CO yields.[131] The main challenge during circulating fluidized bed gasification turns out to be the risk of bed agglomeration.[132] In order to sustain fluidization authors point at the necessity of a fairly low temperature application and continuous kaolin addition.[132] Combustion properties and possible applications of wheat DDGS were studied by Eriksson[133] who summarizes that the slagging tendency of DDGS is higher than for typical wheat straw. The high agglomeration tendency of wheat DDGS in a bench-scale BFB is also reported[87,133]. It was concluded that the agglomeration was due to the formation of ash with a low melting temperature range. In order to avoid ash-related problems during combustion of bioethanol residues, Kersten et al.[134] maintain combustion temperature at 700 °C.

2.5.2   Rapeseed Cake

Some fundamental characterization of thermal properties has been reported by several authors[135-137] and combustion behaviour of rapeseed cake/meal have already been

investigated to some extent[75,138-140]. Standard fuel analyses of the residue from five European RME producers, together with its possible applications have been shown by Eriksson et al.[139]. Combustion of the residue in the fluidized bed boilers was recently a subject of parallel studies performed in 5 kWth bubbling[121,139], 50 kW circulating[138], and 12 MWth circulating[75] fluidized bed boilers. Boström et al.[121], after mono- and co–combustion tests with bark, stated that the residue could be an attractive fuel from the agglomeration point of view, whereas Nevalainen et al.[137] stated that it had a clear agglomeration effect on the bed material when combusted or co-combusted with wood chips. All stressed the importance of potassium -phosphate chemistry during rapeseed cake/meal combustion, which could be counteracted by limestone addition.[75] Co-combustion of rapeseed cake with coal did not show any significant operational problems, neither in a grate furnace[140] nor in a (50 kW) fluidized bed boiler[138].

2.5.3   Palm Kernel Cake

Palm kernel cake has been studied as a potential source of energy by several authors[127,129,141-145]. The literature is mainly related to pyrolysis and only few are related to combustion. Razuan et al.[142] studied the pelletisation of palm kernel cake for energy recovery and also reported full fuel analyses. Wigley et al.[144] studied the influence of palm kernels on deposit formation when co-fired with coal in entrained flow reactor. They concluded that with up to 60 wt% of palm kernels in fuel feed the deposition efficiency was not increased, but the sintering of deposits was. The main elements increasing in the deposits were: potassium, magnesium, and phosphorus. Coda Zabetta et al.[55] reported that 20 wt% of palm kernel (among other agro-biomass) could be co-fired with biomass in units up to 447 MWth.

2.5.4   Fermented Sewage Sludge

Sewage sludge is formed during wastewater treatment. It can undergo anaerobic fermentation which is one of the ways of sludge stabilisation.[24,146] During anaerobic fermentation volatile solids are degraded to a certain degree and converted into biogas. Consequently the sludge volume but also carbon content are reduced. The residual

sludge, called digestate/fermented sewage sludge, is usually sold as compost but could be also combusted.[24]

Fluidized bed combustion of sewage sludge and fermented sewage sludge has a relatively long history.[147,148] It was reported that, due to the low heating value, an auxiliary fuel may need to be co-fired and that a high ash content in sludge results in high ash flow.[149] The sludge ash could be beneficial, however, when sludge is co-fired with alkali-rich fuels, and can lead to significant decrease of alkali chlorides in flue gas and deposits.[150] This could be assigned to aluminium silicates and iron compounds present in sludge that could immobilise potassium and sodium.[151,152] Dry fermented sewage sludge ash is not expected to become sticky at temperatures up to 950 °C.[153]

3   METHODS

The residues of interest were characterized by using laboratory and bench-scale methods, and were tested on a semi-industrial scale. The summary of performed tests is shown in Table 1. Gas release in a single particle reactor (SPR) was studied in *Paper I*. In order to study ash-forming matter, chemical fraction and laboratory sintering tests were applied and discussed in *Paper II*. The bed agglomeration tendency of RC in a bubbling fluidized bed (BFB) reactor was studied in *Papers III-IV* and co-firing of RC in semi-industrial scale circulating fluidized bed (CFB) combustor was studied in *Papers V-VI*.

Table 1 *Methods used in this thesis to characterize the residues.*

method ╲ ╲ residue	laboratory-scale characterization				bench-scale BFB	semi-industrial scale CFB
	section 3.1				section 3.2	section 3.3
	standard fuel analysis *(Papers I-VI)*	combustion in SPR *(Paper I)*	chemical fractionation *(Paper II)*	sintering tests *(Paper II)*	agglomeration test *(Papers III-IV)*	co-firing and use of additive *(Papers V-VI)*
FSS	x	x	x	x	-	-
DDGS	x	x	x	x	-	-
PKC	x	x	x	x	-	-
RC	x	x	x	x	x	x

3.1   Laboratory-scale characterization of the residues (Papers I-VI)

3.1.1   Standard fuel analysis (Papers I-VI)

Ultimate and elemental analyses were performed by an external laboratory. Ultimate analysis was performed according to Swedish and European standards. Carbon, hydrogen, and nitrogen were determined according to ASTM D3178-79 with LECO CHN 600. Sulphur was analyzed with LECO SC-144DR (SS 187177, utg 1), and chlorine with Dionex ICS-90 (SS-187185). Elemental analysis was performed with ICP-AES and ICP-SFMS. For this purpose a fuel sample was first ashed at 550 °C, then digested with $LiBO_2$ and dissolved in HNO_3.

3.1.2   Combustion in SPR (Paper I)

The combustion tests were performed in a single
particle reactor (SPR) in order to study carbon and
nitrogen release from the residues. The setup is shown
in Figure 14. The reactor consists of a quartz tube
inserted in an electrically heated ceramic furnace.
Premixed gases were supplied from the bottom and
the middle of the reactor. Additionally a purging gas
was supplied at the place of sample insertion. The flow
of the gases was controlled by mass flow controllers.
Air was used as an oxidizing gas and nitrogen as a
purging gas. The average residence time for the gases
was around 20 s, while, considering only the product
gases from devolatilization/combustion of the fuel, the
residence time at high temperature was estimated at
about 4 s. The temperature in the reactor was
measured with a thermocouple inserted in the ceramic
wall of the furnace, close to the surface of the quartz

Figure 14 *Quartz tube of the single particle reactor [157].*

reactor in the proximity of the sample placement point. An insertion probe allowed the
sample to be placed on the sample holder in a room temperature environment and then to
be inserted, in a fraction of seconds, into the hot reactor. The reactor was designed and
used mostly for the study of properties of black liquor droplets[154-156] and black liquor
mixtures with biomass[157]. These samples could be placed on a hook and, thus, directly
exposed to the atmosphere. In the present work 10-15 mg of biomass was placed on a
sample holder made of quartz with a porous bottom. A chemiluminescence analyzer was
used for NO detection; a non-dispersive infrared (NDIR) analyzer was used for CO and CO_2
measurement. The measurements were performed for all of the fuels at three different
temperatures relevant for industrial applications: 800, 900, and 1000 °C. Two different

oxygen concentrations, 3 and 10 vol%, were used. Three samples were tested for each fuel at each condition. The content of reduced species (NH_3, HCN, tar-N) were not analyzed.

3.1.3   Chemical fractionation (Paper II)

Principals of chemical fractionation analysis used in this work are described in detail in literature[158-162]. This method has been developed for coal[163], later adapted for biofuels[57] and modified[46,179]. It is applied to determine the chemical forms of the ash-forming matter in fuels. Chemical fractionation is based on selective consecutive leaching by water (H_2O), 1M ammonium acetate (NH_4Ac), and 1M hydrochloric acid (HCl). Subjecting the untreated fuel samples to the increasingly aggressive solvents produces a series of
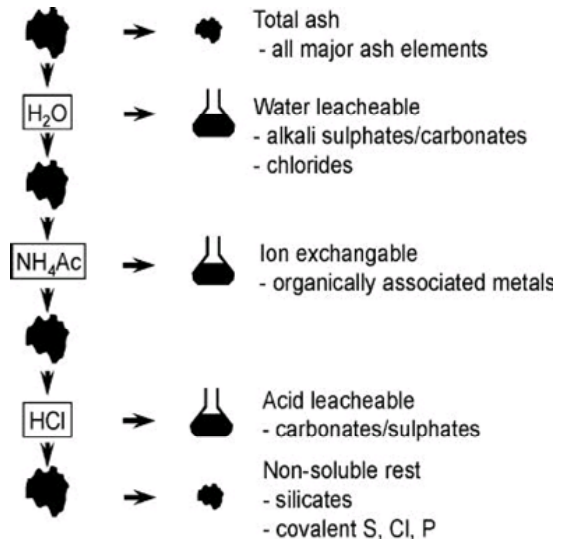
Figure 15 *Chemical fractionation analysis [56] based on [178].*

four fractions. The untreated samples, the three liquid fractions, and the remaining solids are analyzed for the elemental composition by an external laboratory with ICP-AES and ICP-SFMS. A scheme of the procedure is shown in Figure 15. Analysis was performed on a single fuel sample. The reliability of the results is indicated with the mass balance closure. This means the concentration of an element in an untreated fuel sample compared to the sum of the element concentrations in the four fractions from the chemical fractionation. The four fractions are: water leachable, ion exchangeable, acid leachable, non-soluble rest.

3.1.4   Sintering tests (Paper II)

The ash sintering tendency of the fuels was investigated using three different tests: microsample sintering, pellet sintering, and standard ash sintering (CEN/TS 15370). Laboratory ash prepared at 550 °C was used in the pellet sintering and standard ash sintering tests, while the original fuels were used for the microsample sintering test.
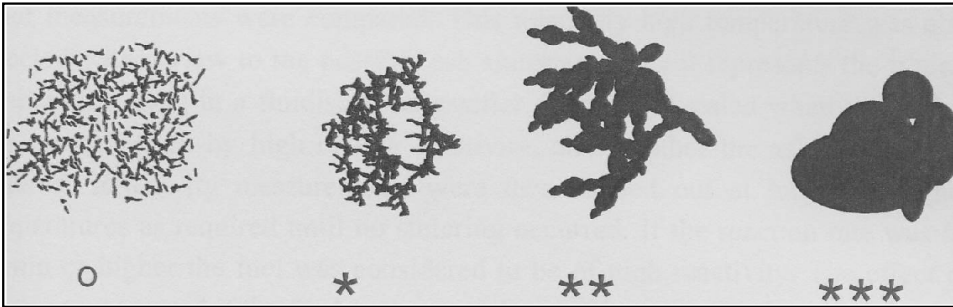
Figure 16 *Classification of sintering tendency [164].*

The degree of **microsample sintering** for fuel samples was investigated using a thermogravimetric analyzer (TGA) and an optical microscope equipped with a digital camera. The fuels were ground (particle size less than 1.0 mm) to ensure the homogeneity of the samples. Approximately 15.5±0.3 mg of the fuel sample was placed in the hot reactor at a stabilized temperature. The airflow was kept constant at 50 ml/min. Three samples were tested for each fuel at each temperature (550 °C and 1050 °C). The sample was removed after 25 min and cooled to room temperature. A picture was taken with a digital camera through the optical microscope at three different magnifications: 1.6, 3.2, and 5.0. Based on the pictures, the ash samples were classified according to four classes of sintering defined by Moilanen et al.[164] (Figure 16). Unsintered ash residue that resembles the original fuel particles is marked "0". There are two classes of partly sintered ash particles. The first, labelled with one asterisk, describes a sintered sample in which individual particles of the original unsintered sample can still be observed. In the second, labelled with a double asterisk, individual particles of the original sample can no longer be distinguished. Completely sintered ash particles are labelled with three asterisks.

Pellet sintering tests were based on compression strength measurement tests described in detail by Hupa et al.[165] and Skrifvars[166]. The main stages of the method are shown in Figure 17. The standard ash was pelletized into 8.0 mm-high cylinders with a diameter of approximately 8.3 mm. The pelletizing pressure applied to all the pellets was the same (approx. 40×10^5 Pa); it was determined by finding the minimum measurable pressure necessary to pelletize the ash. After preparation, the pellets were subjected to heat treatment for 4 hours at various temperatures in the range between 350 °C and 950 °C in a tube furnace with a constant

synthetic air (80% N_2 and 20% O_2) flow of 3.3 Nm^3/s. Three pellets were prepared for each temperature. After heat treatment, the pellets were removed and cooled to room temperature in desiccators. The size of each pellet was checked to calculate the compression strength per mm^2. The compression strength was measured with a standard crushing device.
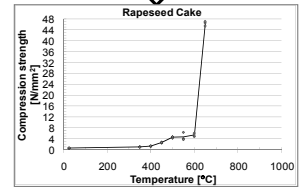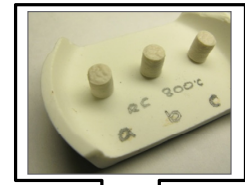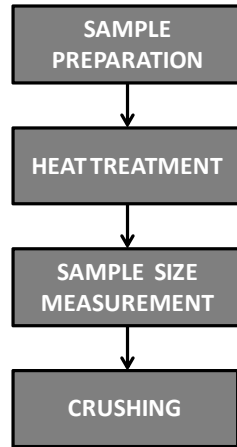
Figure 17 *Pellet sintering test.*

Standard ash sintering test was performed according to the procedure described in CEN/TS 15370[167]. Ash pellets with a diameter equal to their height (3.0 mm) were subjected to heat treatment at a controlled heating rate up to 1500 ºC; the heating rate between 500 ºC and 1500 ºC was 5 ºC/min.

Images of the pellet during heating were recorded and evaluated automatically with an image analysis routine written in MATLAB, and they were used to identify the phases in the ash melting process, as described in Figure 18. The transitions were determined based on the shrinkage of the pellet area. The initial shrinkage temperature corresponds to a 5% shrinkage of the cross-sectional area. The deformation temperature, defined in the standard as a 15% change in the shape factor, could not be detected for the square-like cross sections, so these are not included in the results. Three replicates were performed for each fuel.
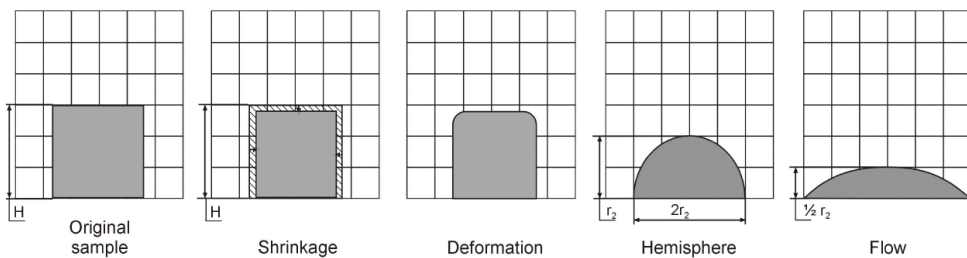
Figure 18 *Phases in the ash melting process (original shape = shape and size at 550 ℃) according to [167].*

3.2 Bed agglomeration tests in a bench-scale BFB (Paper III-IV)

3.2.1 Experimental set-up

The experiments for *Papers III-IV* were carried out in a bench-scale 5 kW bubbling fluidized bed reactor (BFB), described in detail by Öhman and Nordin[168] (Figure 19). The stainless steel reactor is 2 m high with an inner diameter of 100 mm in the bed section and of 200 mm in the freeboard section. The maximum temperature that can be reached is 1045 °C (in the bed). A constant temperature is achieved by using preheated primary air, in conjunction with electrical heaters in the freeboard section. A perforated stainless steel plate at the bottom of the fluidized bed with 1% open area functions as an air distributor. The temperature and pressure drop in the bed

Figure 19 *Schematic view of the bench-scale BFB (5 kW); courtesy of Alejandro Grimm (Luleå University of Technology, Division of Energy Engineering).*

were continuously monitored using two thermocouples and two pressure probes.

Experiments were conducted using two fuels: spruce bark, and rapeseed cake. The samples were ground, and eleven different mixtures were prepared, with the proportion of bark ranging from 0 to 100 wt%. For each mixture, approximately 40 kg of ground material was homogenized in a concrete mixer before pelletizing. The bed agglomeration test was carried out for all mixtures. Each experiment could be divided into two stages: combustion and agglomeration (Figure 20).

Stage 1 is combustion of continuously fed fuel. This is followed by stage 2, a controlled fluidized bed agglomeration test. During the first stage, approximately 4-5 kg of fuel mixture, continuously fed into the reactor with a screw feeder, was burned for 8 h at 800

°C. Bark and rapeseed cake have a similar energy content, so a constant fuel input guaranteed a constant energy output of 3.3 kW ± 0.3. For each experimental run, 540 g of fresh quartz sand (>98% SiO_2) was used, with an initial particle size in the range of 200-250 μm. The excess oxygen level was maintained at
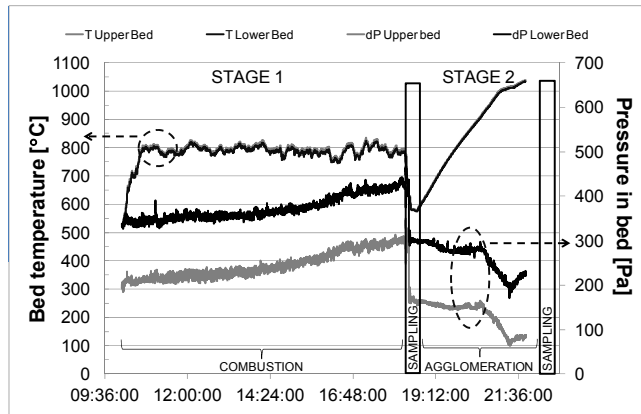
Figure 20 *Stages in controlled agglomeration: bed temperature and pressure versus time for 90 wt% bark and 10 wt% rapeseed cake.*

8% dry flue gas for all the experiments, and the air flow was kept constant at 80 Nl/min. During the combustion phase, the fluidization velocity was kept 10 times higher than the minimum fluidization velocity, corresponding to about 1 m/s. After 8 h of combustion, the fuel feed was stopped, and a sample of bottom ash was collected. The air flow was minimized to 30 Nl/min, and combustion of propane gas in a chamber below the primary air distributor plate was initiated. During the agglomeration tests, propane was burned below the air distribution plate, making it possible to achieve the desired mixing of gases and to maintain a combustion atmosphere in the reactor. Then, the bed was heated at a constant rate of 3 °C/min until defluidization was achieved. After reactor cooled down sample of agglomerates was collected.

3.2.2 Samples and analyses

The recorded temperature and pressure curves were analysed to determine the initial and the total defluidization temperatures. The initial defluidization temperature is the temperature at which changes in the bed pressure are first observed and it probably indicates that the growth of agglomerates and/or slagging begin to take place. In case where the pressure curves were constantly declining during the 8-h combustion stage, initial defluidization was said to occur during combustion. When the pressure curves were stable or increasing during the combustion stage, the initial defluidization temperature

was determined based on the pressure curves for the agglomeration stage: it is defined as the point of intersection of two tangent lines to the differential pressure curves. The total defluidization temperature refers to the temperature at which no fluidization is observed: it is defined as the

Figure 21 *Bed defluidization temperatures indicated on the temperature and pressure profile for test 60 wt% of bark and 40 wt% of rapeseed cake.*

first temperature at which the pressure curve reaches its minimum (Figure 21).

Cross-sections of both collected bottom ash samples after stage 1 and 2 were studied by means of SEM/EDX. With the sample collected after the combustion stage (STAGE 1) the layers on the bed particles were studied. Samples after the agglomeration stage (STAGE 2) were used to study the agglomerate necks. For the purpose, the bed particles were embedded in epoxy resin, and after drying were ground with silica carbide grinding paper to a obtain smooth surface that was covered with thin carbon coating.

SEM/EDX point analyses were carried out for two types of ash samples: fuel-derived ash found in bottom ash sample collected after stage 1, and fly ash. Fuel-derived ash particles ($d_p < 200$ µm) were sieved from the bottom ash sample. Fly ash samples were collected from the cyclone ($d_p < 10$ µm). For SEM/EDX analyses ash samples were mounted on carbon tape and covered with a thin carbon layer. From 50 to 90 data points in each bottom ash sample were analysed for the following experiments: B0, B10, B50, B60, B70, and B90. For pure bark combustion test (B100) only a few bottom ash particles could be found and 12 data points are given for this test. Between 60 to 100 data points were analyzed for fly ash samples for the following tests: B0, B10, B50, B70, B90, and B100. All together approximately 470 data points from bottom ash and 480 data points from fly ash samples were analysed.

3.3 Co-firing in a semi-industrial scale CFB (Papers V-VI)

3.3.1 Experimental set-up

Combustion tests at a semi-industrial scale were performed in a 12MWth circulating fluidized bed (CFB) boiler. The schematic diagram of the boiler is shown in Figure 22. The combustion chamber is 13.6 m high and has a cross section of 2.25 m². Fuels are mixed before being fed through the fuel chute. Primary air is introduced to the bottom of the bed and secondary air 2.2 m above the bottom plate. The bed temperature during
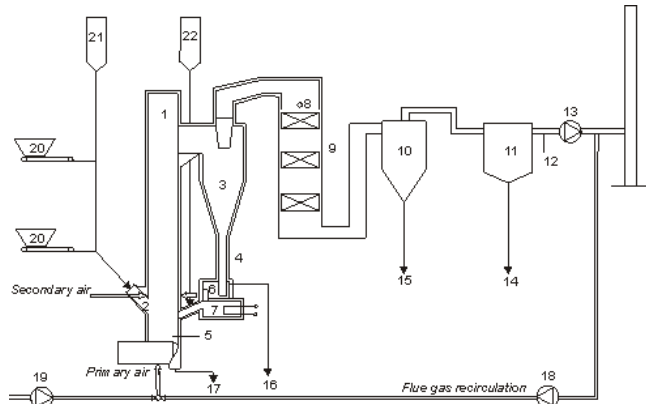
Figure 22 *The schematic diagram of the 12 MWth CFB boiler at Chalmers University of Technology:*
(1) combustion chamber; (2) fuel feed chute; (3) primary cyclone; (4) particle return leg; (5) bottom ash sampling spot; (6) loop seal; (7) heat exchanger; (8) deposits sampling spot and position of IACM upstream of the convection pass; (9) convection pass; (10) secondary cyclone; (11) bag house filter; (12) flue gases measuring spot; (13) flue gas fan; (14) bag house filter ash sampling; (15) secondary cyclone ash sampling; (16) recirculating material sampling spot; (17) bottom ash removal; (18) flue gas recirculation fan; (19) air fan; (20) fuel bunkers; (21) sand bin; and (22) limestone bin.

the experiments presented in this work was held at approximately 850 °C at the bottom and at approximately 860 °C at the top of the bed. The excess air ratio was held at 1.21. Fly ash samples are captured in secondary cyclone and bag filter ash. Secondary cyclone consists of ash particles >10 µm.[169] This coarse mode of fly ash is mainly formed via entrainment of ash particles with the flue gas. In the bag filter ash particles <10 µm can be found. These particles could originate from the fine entrained ash fraction but most probably are mainly formed during condensation or nucleation of vapours.

During the tests, the boiler was operated at approximately 6.0 MW thermal. The flue gas temperature was approximately 830 °C when entering the convection pass, and the fly ashes were separated in the secondary cyclone and the bag house filter, where the temperature dropped to about 150–160 °C. There is approximately 3000 kg of bed

material in the system (50% in the riser section and 50% in the cyclone leg and particle seal). During all tests, sand consisting of 98.9% silica (SiO_2) was used as bed material, with a particle diameter of 106-125 μm. The limestone was taken from Ignaberga in the south of Sweden and more than 93% of it is calcium carbonate.[170] Bottom ash, circulating material, and fly ash samples were collected after approximately 12 h and at the end of each co-combustion test.

During the tests rapeseed cake (RC) pellets were co-fired with two base fuels: wood or coal. For the wood case, a mixture of wood chips produced from spruce grown in the south of Sweden, and wood pellets (WP) produced from pre-dried sawdust originating from pine and spruce; was used. Two 12 hour tests with and without limestone addition were carried out. In both tests approximately 15% on an energy basis of rapeseed cake was used. During the tests with coal, South African bituminous coal was used as a base fuel. Two 22-23 hour tests were carried out with limestone as a varying parameter. Approximately 25% of rapeseed cake on an energy basis was co-fired. A test without limestone followed a test with limestone addition with a 1.5 h break, during which only coal was combusted.

3.3.2 Samples and analyses

Samples from all outgoing solid material streams, namely: bottom ash and fly ash samples, were collected at the end of each test. These samples were analyzed quantitatively by means of ICP-AES according to ASTM D3683 and ASTM D3682 by an external laboratory. After the bag filter (12 in Figure 22), the emission of HCl was measured by means of Fourier transform infrared (FT-IR) and SO_2 with a non-dispersive ultraviolet (NDUV) analyzer. The quantitative analyses of the incoming and outgoing solid streams and emission measurements were used to calculate elemental flows.

Agglomeration characteristics of each fuel mixture were studied by means of SEM/EDX. For this purpose the cross sections of bottom ash particles, collected 0.7 m above the nozzles (5 in Figure 22), were prepared. First the bed particles were embedded in epoxy

resin, and after drying were ground with silica carbide grinding paper to obtain a smooth surface that was covered with a thin carbon coating.

Deposit samples were collected on steel rings (outer diameter 38 mm) that were fitted on an air-cooled probe situated in the middle of the flue-gas stream before the convection pass (8 in Figure 22). The surface temperature of the steel rings was set at 480 °C during the 12-h tests to simulate superheater tubes. The rings were weighed before and after exposure to the flue gas. The difference in weight was used to calculate the rate of deposit build-up (RBU). Semi-quantitative analyses of the deposit samples were performed by means of SEM/EDX.

Additionally, at the beginning of the convection pass (8 in Figure 22) gaseous HCl and SO_2 concentrations were measured using FT-IR. In addition, the concentration of gaseous alkali chlorides was continuously measured at this position using the in-situ alkali chlorides monitor (IACM) developed by Vattenfall.

4 RESULTS AND DISCUSSION

4.1 Laboratory-scale characterization of residues

4.1.1 Characterization with standard fuel analysis (Papers I-VI)

Biomass has a significantly lower heating value than coal (Table 2). This is due to the low carbon and high oxygen contents in biomass fuels.

The different origins of the tested residues are already clearly visible from the data reported in Table 2. Dried distillers' grains with solubles (DDGS), palm kernel cake (PKC), and rapeseed cake (RC) present similar content of C, H, and O, while fermented sewage sludge (FSS), because of a completely different origin, differ greatly in composition. While the agricultural residues have a carbon content of around 50 wt% db, which is similar to woody fuels, the content of carbon in the FSS is lower than 30 wt% db. The content of nitrogen in all tested residues is definitely higher than in other biomass materials or even coals. Nitrogen concentration between 2.4 to almost 6 wt% db warns of possible high NO_x emissions. Sulphur in FSS and RC is significantly high (0.7-1.2 wt% db). The release of SO_2 was not further studied in this work. The ultimate analysis gives an indication of emissions, but, cannot accurately predict the combustion in a large scale fluidized bed boiler.

Elemental analysis of the residues and reference fuels is shown in Table 3. In contrast to fossil fuels, biomass contains many fewer minerals and consists more of the nutrients required for the proper development of living cells. Sulphur and chlorine are shown in

Table 2 *Ultimate analysis and energy content of the residues and reference fuels (fuels used in Papers I-VI)*

	dry basis	COAL	RC	DDGS	PKC	FSS	SPRUCE BARK	WOOD CHIPS	WOOD PELLETS
LHV	MJ/kg	27.1	20.7	18.5	18.1	9.7	19.8	18.7	18.9
C		69.3	49.9	46.7	47.1	26.5	52.3	49.9	50.6
O		10.0	29.9	36.2	38.3	14.9	36.6	43.3	42.8
H		4.4	6.9	6.7	6.5	5.9	5.7	6.0	6.1
N	wt%	1.8	5.1	3.9	2.5	3.2	0.4	0.2	0.1
S		0.5	0.7	0.3	0.2	1.2	0.0	0.0	0.0
Cl		<0.05	0.26	0.18	0.18	0.07	0.02	<0.05	<0.05

Table 3 *Elemental analysis of the residues and reference fuels (fuels used in Papers I-VI).*

	dry basis	COAL	RC	DDGS	PKC	FSS	SPRUCE BARK	WOOD CHIPS	WOOD PELLETS
P		915	11500	8750	6090	33900	506	120	56
Si		32900	261	6580	4090	33200	4642	346	165
Al		20200	43	75	1370	13900	1006	207	37
Mg		2030	4500	3090	2970	4000	790	224	160
Ca	mg/kg	7470	7040	1440	3930	28900	9648	1100	783
Na		637	4660	1330	145	2630	356	50	29
K		1310	12300	11900	6790	4410	2192	594	432
Mn		58	60	44	277	530	479	166	112
Fe		2690	152	156	4360	114000	497	204	44
Ti		1180	4	5	53	1400	38	8	2

Table 2. Even though these two elements form gaseous species (SO_2 and HCl), they are often bound in ash. For coal, the main ash-forming elements are silicon and aluminium, which mainly originate from different clays and impurities. On the other hand for biomass the main elements are Ca, Mg, K, P, and S. These elements are considered to be macronutrients, which are essential for plant growth. Silicon, aluminium, and sodium are considered non−essential for plant growth (review by Werkelin[50] based on biological studies[113,171,172]). The studied residues, compared to traditional woody biomass and coal, contain very high concentration of phosphorus. The influence of phosphorus on the ash chemistry will be therefore further studied in this thesis.

4.1.2 Carbon and nitrogen release during combustion in SPR (Paper I)

When a solid fuel enters a hot fluidized bed the volatile compounds are released rapidly and some remain in the solid char. The remaining compounds are released during slow char oxidation stage (Figure 10). Volatile carbon and nitrogen follow different conversion routes than char bound elements. Their different oxidation pathways, which were described in literature[173-175], result in different secondary reactions. Therefore the division between volatile and char release is of importance for determination of fate during combustion and emission prediction. In this work the single particle reactor (Figure 14)

allowed us to study the release of carbon (as CO and CO_2) and nitrogen (as NO) and to differentiate between two combustion stages. The results are shown as the average of three measurements. In order to determine different contributions of volatile versus char emissions, the curves obtained from the analyzers were fit with two Weibull-type distributions representing the devolatilization and char burning contributions using a least-squares method. The total release of carbon (as CO and CO_2) resulted in mass balance closures between 80 and 100%; the difference in the mass balances was most likely
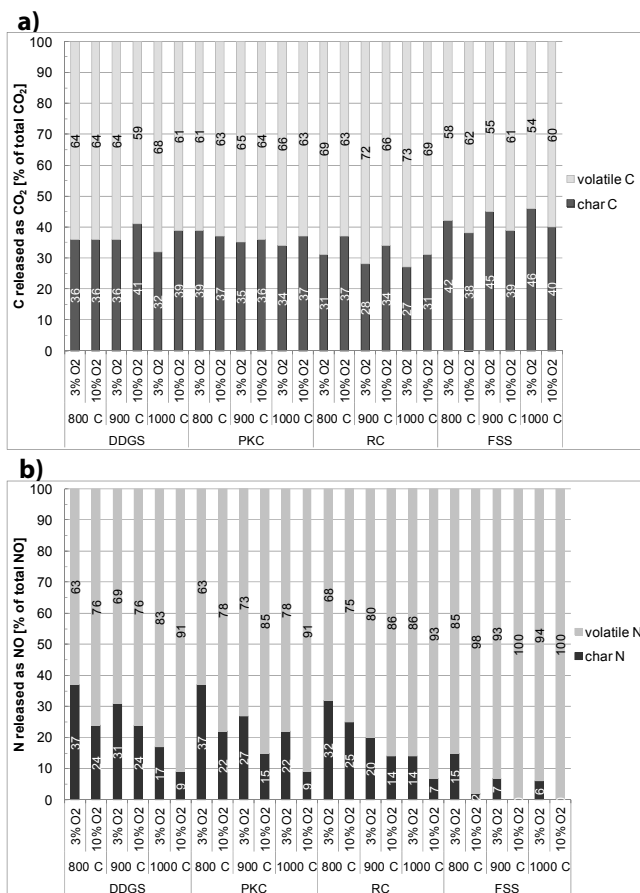
Figure 23 *Carbon a) and nitrogen b) release during devolatilisation and char oxidation (Paper I).*

due to the formation of soot. The release of fuel N as NO at all studied conditions was below 30% of initial nitrogen content in the fuels.

Figure 23 a) shows the division of released carbon. Quite homogeneous behaviour for all fuels can be observed. The percentage of volatile carbon ranged from 55 to 60% for the FSS and went up to 65-70% for the residue materials. This is in agreement with the higher carbon and volatile content of the residues (*Paper I*). On the other hand nitrogen does not show such a uniform behaviour (Figure 23 b). With increasing temperatures, it appears that a decrease of NO released during char oxidation occurs. At low temperatures most of the fuels released around 60-70% of their total released fuel N as NO during the

devolatilization stage. At higher temperatures, almost all measured NO was released during the devolatilization stage. The values are comparable to previous studies[176,177] reporting volatile N values in the range of 60-70% for different types of biomass materials.

The performed measurements show how, despite the high nitrogen content of these fuels, most of the formed NO was released in the few seconds of devolatilization, so that the reduction of NO with radicals from NH_3 and HCN could be effective even without the application of air staging. The overall emissions of NO are the results of simultaneous formation and reduction of nitrogen oxides during combustion.

4.1.3 Determination of ash-forming matter (Paper II)

Chemical fractionation was applied to all studied residues in order to determine how ash-forming elements are bound in fuel.[178] Chemical fractionation divides ash-forming matter into: water fraction, ammonium acetate fraction, acid fraction, and rest fraction.[179] As reported by Werkelin et al.[50] the water-soluble fraction in woody biomass fuels consist mainly of KCl, KH_2PO_4, and K_2SO_4. Ammonium acetate fraction consists of organically associated metal ions. The acid and rest fractions consist mainly of minerals and also some parts of covalently bound non-metals (Figure 15).

The chemical fractionation results for the residues studied in this work are shown in Figure 24. The ash-forming matter of FSS occurs mainly in the form of iron phosphates, which are likely present because iron sulphate is used during wastewater treatment processes for the precipitation of phosphorus. The presence of aluminium silicates in the form of zeolites can also be indicated; the aluminium in the hydrochloric acid soluble fraction most probably originates from the dealumination of zeolites in the HCl solution. The ash-forming matter of DDGS is mainly leached in water, indicating the presence of highly soluble salts of alkali metal phosphates and chlorides. In addition, some mostly insoluble silicon is detected. The origin of the silicon might be explained by contamination with sand. Some silicon could also have accumulated in the barley grain during plant growth. The presence of sulphur in the unleached residual fraction indicates that it is covalently bound to organic matter. In PKC, insoluble aluminum silicates,

probably contaminants or residues from the production process occur together with highly soluble potassium, phosphorus, and chlorine. Low concentrations of silicon are found in RC, in which the ash-forming matter consists of alkali metals, phosphorus, sulphur, and chlorine; they appear mainly in the fraction leached by water, indicating the presence of simple salts like alkali metal chlorides, sulphates, and phosphates. A substantial amount of sulphur was found in the residual fraction, suggesting that RC also contains covalently bound sulphur. Acid and ammonium acetate soluble phosphorus is assumed to occur in the form of phytic acid salts.

Ash-forming matter undergoes different transformations in combustion, such as oxidation (e.g., the oxidation of organic sulphur to SO_2); chemical reactions of, for example, reactive species with bed material; and thermal decomposition (e.g., the calcination of calcium carbonates or loss of structural water from minerals or crystals), depending on how it is combined with other constituents.[178] An understanding of the association of the ash-forming matter in fuels serves as a starting point for understanding its subsequent transformations.
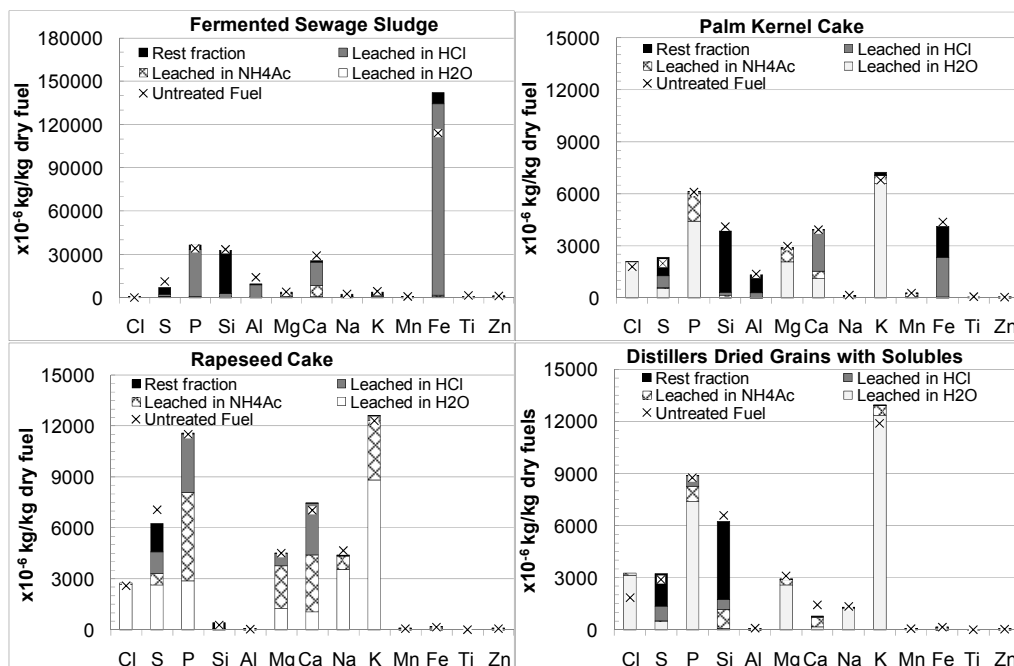
Figure 24 *Chemical fractionation results for the residues (Paper II).*

4.1.4 Determination of sintering tendency (Paper II)

Based on microsample sintering tests, DDGS exhibits the highest sintering tendency. During the microsample sintering test (Table 4), at 950 °C, DDGS already formed a molten amorphous phase and the sample could not be removed from the crucible. For RC, cake-

Table 4 *Summary of microsample sintering test results (Paper II).*

Temperature [°C]	RC	DDGS	PKC	FSS
550	0	0	0	0
750	*	*	0	0
850	*	**	*l	*l
950	**	molten	*	**
1050	***	n/a	**	***

n/a-data not available

like sintering could first be observed at 750 °C. However, further progression of the ash sintering could be observed at 950 °C. Differences in the ash sintering tendency arise from
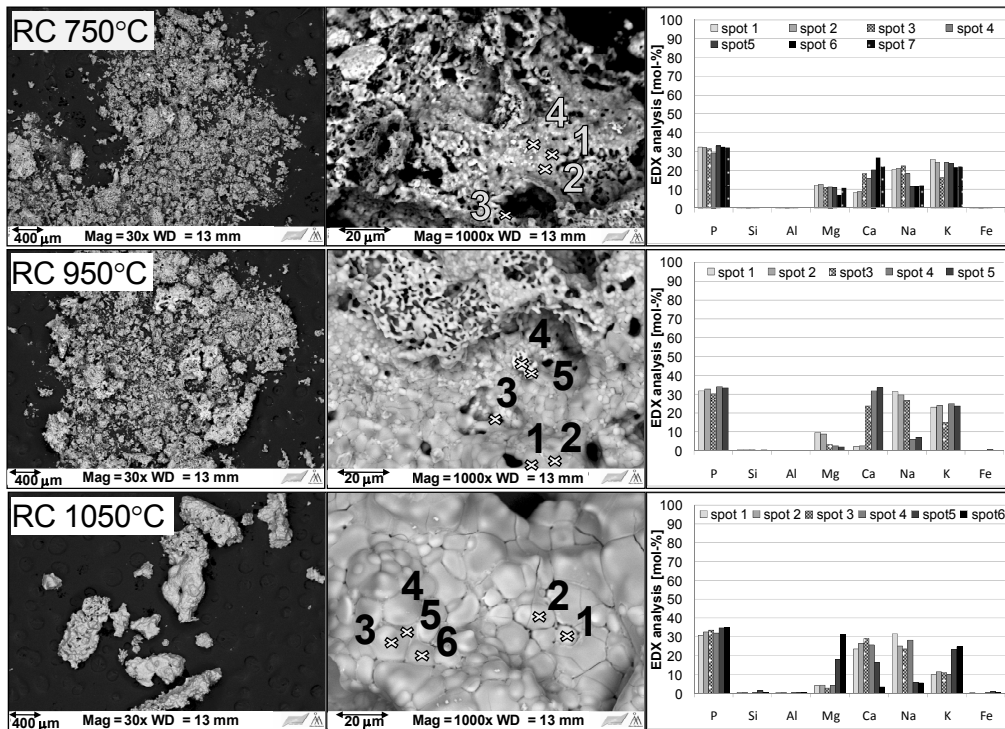
Figure 25 *SEM/EDX point analyses of rapeseed cake (RC) after the microsample sintering test. Results are shown on oxygen and carbon free basis (Paper II).*

differences in the ash-forming matter and the way it is combined. The two fuels with the lowest sintering temperatures, DDGS and RC, have the highest concentrations of water-soluble alkali metals and phosphorus. The PKC and FSS exhibit the lowest sintering tendency. The determined sintering temperatures indicate the properties of ash. They do not directly correspond to bed sintering temperatures, however, during fluidized bed combustion.

The composition of palm kernel cake is similar to that of RC. Their sintering tendencies differ significantly, however, and that could be attributed to the smaller ratio of water-soluble alkali metals to earth alkaline metals in PKC; another possibility is the influence of the Al-Si in the fuel sample. Phosphate species can interact with the silicate phases, but the interaction needs to be further clarified.[86] The chemistry of studied FSS is dominated by iron oxides and, as concluded by Wang et al.[180], the appearance and disappearance of Fe_2O_3 in ash was the leading factor affecting the sintering of sewage sludge ash when $Fe_2(SO_4)_3$ was used at a wastewater treatment.

SEM/EDX results of microsample sintering test are introduced in detail in *Paper II.* Here the results for RC are discussed (Figure 25). The SEM/EDX results support that RC sintering tendency is driven principally by the presence of alkali metal and earth alkaline phosphate particles. Based on literature findings and this research a summary of ash melting behaviour is shown in Figure 26. The melting behaviour of the two kinds of phosphate was discussed by Lindström et al.[85], who studied the slagging characteristics of phosphorus fuels with and without limestone addition in a residential cereal burner. They concluded that limestone, as a source of calcium, contributes to the formation of high-
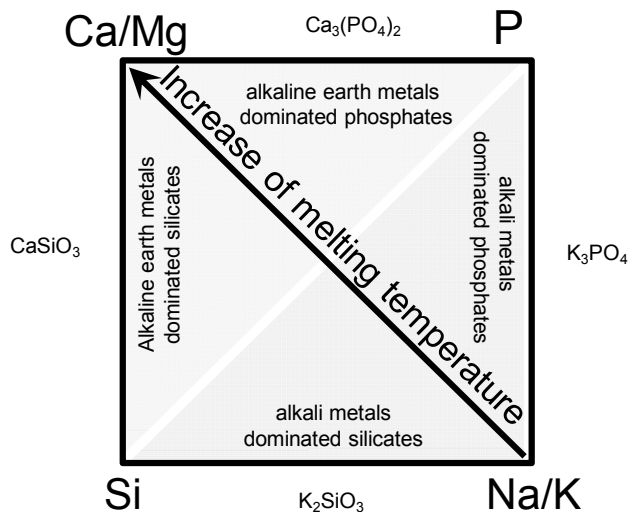
Figure 26 *Summary of melting behaviour.*

temperature melting calcium potassium phosphates. The formation of high melting phosphates in a fluidized bed was investigated by Barišić et al.[75], who reached a similar conclusion. Steenari et al.[86] reduced the sintering tendency of laboratory ash of rapeseed cake with the addition of limestone. They pointed out that a high K/Ca ratio can be associated with low temperature ash sintering and melting for phosphorus-rich fuels. The increase of the melting temperature with the content of earth alkaline metals for both: silicates and phosphates; could be inferred from the results (Figure 26). However, the interactions of phosphates and silicates are also of importance, and should be further studied. These interactions could most probably result in lowering the first melting point and result in the formation of strongly sintered ash.

The overall sintering trend exhibited by the four fuels introduced in Table 4 is in agreement with that for the pellet sintering tests (Figure 27) and with the results from the standard ash sintering (Figure 28), with the initial sintering temperature increasing in the following order: RC<DDGS<PKC<FSS.
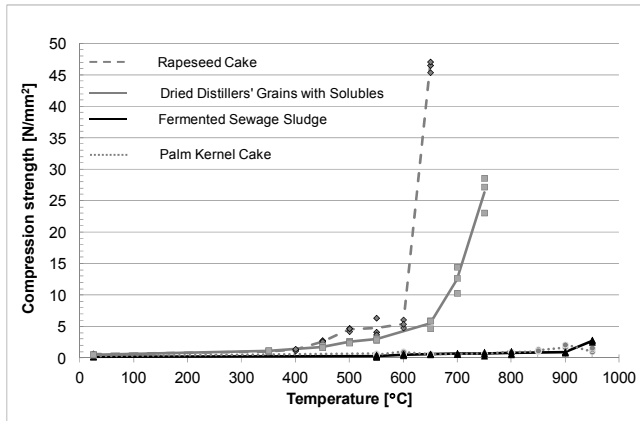
Figure 27 *Pellet sintering test results (Paper II).*

There are some disagreements, however, regarding the initial sintering temperatures. Pellet sintering tests suggest that the onset of sintering takes place at lower temperatures for RC and DDGS than were identified during the microsample
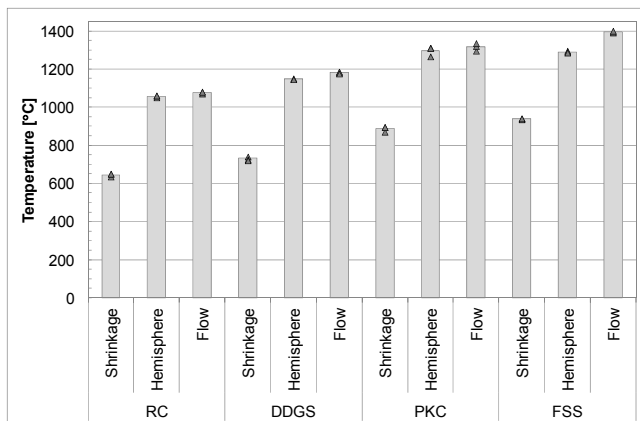
Figure 28 *Standard ash sintering test results (Paper II).*

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sintering test and the standard ash sintering test. The initial sintering temperatures for FSS and PKC are similar for all the tests. The initial sintering for PKC and FSS is expected to occur at approximately 900-950 °C. However for the pellet sintering test no hard sintering was observed in the temperature range, making determination of the onset temperature difficult.

The lowest initial sintering temperatures were observed for RC and DDGS, and for the three sintering methods. They are below 800 °C, suggesting that these fuels should not be combusted alone, without precautions against ash-related problems, no matter what the combustion technology. The PKC and FSS samples do not exhibit significant sintering below 900 °C, which could be interpreted to mean that when the combustion temperature is below 900 °C no significant ash-related problems will occur. However this temperature corresponds to the fuel ash sintering tendency, and does not take into consideration the influence of other parameters related to the combustion technology, e.g. bed material in a fluidized bed.

4.2   Bed agglomeration tests in a bench-scale BFB (Papers III-IV)

4.2.1   Determination of bed defluidization temperatures (Paper III)

The agglomeration tendency of mixtures of rapeseed cake and spruce bark was determined using controlled fluidized bed agglomeration tests. The initial defluidization temperatures (IDT) and the total defluidization temperature (TDT), described in section 3.2, were plotted as functions of the mixture composition (Figure 29). The inaccuracy of ±30 °C was determined in previous studies[168] and is included in the Figure. The TDT indicates the temperature at which the formation of agglomerates leads to the complete collapse of the bed and loss of fluidization. Rapeseed cake showed a strong agglomeration tendency, and total defluidization occurred during the combustion stage (800 °C). At the other extreme, the TDT for bark was above 1045 °C, so it could not be measured due to the limitations of the experimental set-up. These results are in agreement with findings from previous studies on the agglomeration tendency of bark.[139] In Figure 29 the initial defluidization temperature (IDT) is also indicated. At this temperature the growth of agglomerates and/or slagging begins to take place. The IDT in this study was sometimes as much as 200 °C lower than the total defluidization temperature.
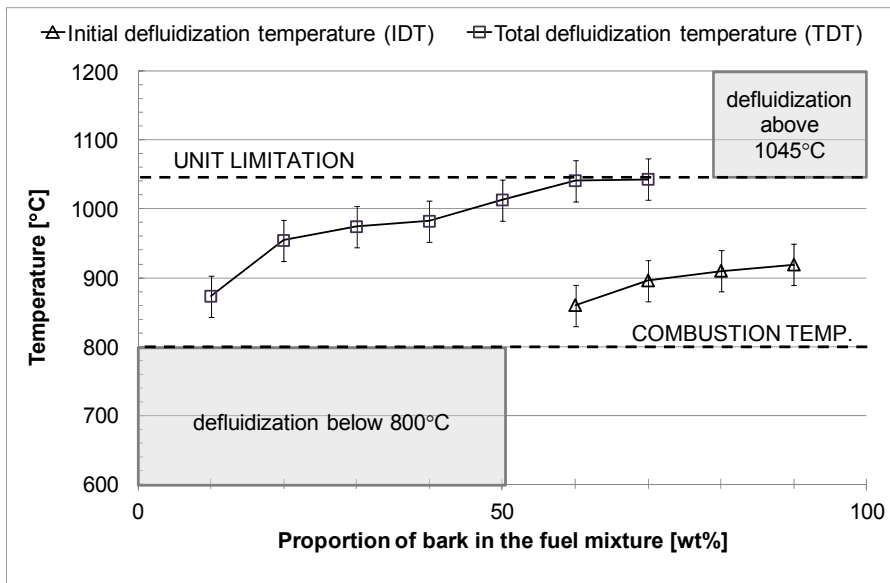
Figure 29 *Bed defluidization temperatures versus proportion of bark in the fuel mixture (Paper III).*

The defluidization temperatures of the fuel mixtures increase with increasing proportion of bark. The change in the trend in the graph of the IDT occurs for 60 wt% of bark. For mixtures dominated by RC ash (0-50 wt% bark), a constant decline in the pressure curve can already be observed during the combustion stage (800 °C). Accordingly, it is reasonable to suppose that initial defluidization occurs during combustion.

4.2.2   Correlation between defluidization temperatures and ash-forming matter (Paper III)

Three molar ratios were used to describe ash-forming matter: (K+Na)/(Ca+Mg), (Ca/P), and (K+Na-P)/(K+Na), and were plotted as a function of fuel mixture (Figure 30). A correlation between the molar ratios, the defluidization temperatures, and the formation of the inner reaction layer is shown. The molar ratios which correspond to the mixture with significantly higher defluidization temperatures compared to rapeseed cake mono-combustion (60 wt% bark) are further discussed. Calcium to phosphorus (Ca/P) molar ratio in the mixture is approximately 1.3 and the molar ratio of alkali metals to alkaline earth metals (K+Na)/(Ca+Mg) is 0.8. These molar ratios indicate an increase of alkaline metals in the phosphate compounds. An increased content of Ca in a Ca-K-P system may shift the
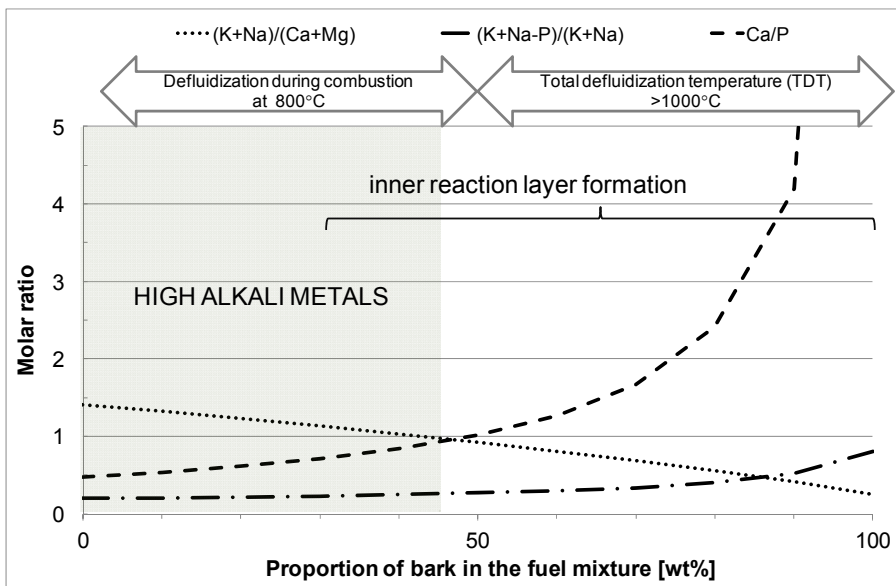
Figure 30 *Molar ratios versus the proportion of bark in the fuel mixture (Paper III).*

first melting temperature to over 1000 °C.[85] This is in agreement with the defluidization temperature result for the mixture with 60 wt% of bark (TDT ~1045 °C).

Another shown molar ratio is (K+Na-P)/(K+Na). It indicates the amount of alkali metals that may be available for the formation of alkali silicates, -chlorides or -sulphates. The strong affinity of phosphorus towards alkali metals was reported by Boström et al.[121,181] and alkali metals phosphates are formed preferably if both silicon and phosphorus are present. The molar ratio (K+Na-P)/(K+Na) was below 0.3 for mixtures up to 60 wt% bark in fuel mixture. An inner reaction layer, however, can be already observed in mixtures with as low as 30 wt% of bark (Figure 30), indicating the possible reaction of alkali phosphates with silica grains as was suggested by Barisič et al.[75]. The formation of an inner reaction layer has been well reported in literature in respect to agglomeration mechanisms for woody fuels. This layer is formed when alkali metal compounds are reacting with bed material particles, leading to the formation of potassium silicates, whose first melting point could be as low as 750 °C. The resulting inner reaction layer on the bed material particles leads to viscous flow sintering. It is discussed in more detail in *Paper III*.

4.2.3   Fly and bottom ash composition before agglomeration stage (Paper IV)

The composition of ash particles found in the samples from combustion of bark (B100) and rapeseed cake (B0) are shown in Figure 31. During bark combustion (B100) hardly any fuel-derived ash particles could be found in the bottom ash samples and the composition
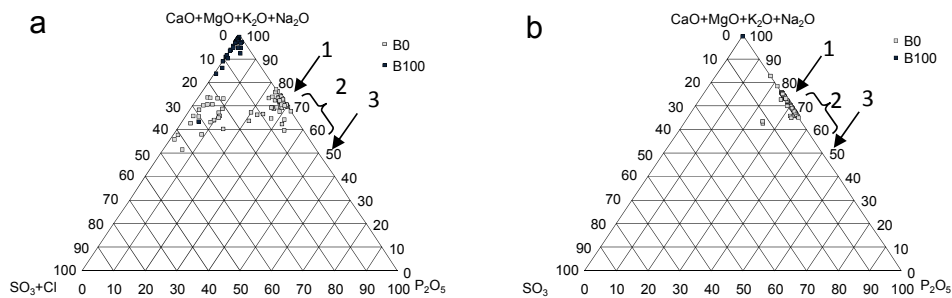
Figure 31 *Composition of fly ash (a) and bottom ash (b) samples for 0 wt% bark (pure rapeseed cake) and 100 wt% bark determined by SEM/EDX. Here only points with SiO₂ <10 mol% are shown (Paper IV).*
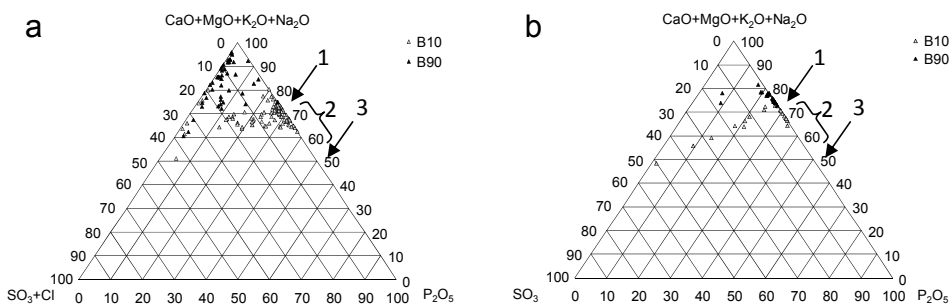
Figure 32 *Composition of fly ash a) and bottom ash b) samples for tests B10 and B90 based on SEM/EDX. Here only points with SiO_2 <10 mol% are show (Paper IV).*

of a single bottom ash particle is shown in the figure. Combustion of bark results mainly in the formation of fine particles collected in the cyclone (fly ash with dp <10 μm). The composition of fly ash formed during combustion of bark is found in the top corner of the triangle (Figure 31 a). These points almost entirely correspond to calcium compounds (in the diagrams expressed as oxide). Calcium compounds occurring in biomass ash are CaO, $CaCO_3$, and $Ca(OH)_2$. However, in this study these compounds were not distinguished and are described with CaO. Some calcium sulphate and chloride also formed. Composition of ash for fuel mixtures with high proportion of RC (B10) and high proportion of bark (B90) is shown in (Figure 32). Higher amount of sulphates and chlorides formed for test B90 when compared to the pure bark test (B100). This could be explained with 10% of rapeseed cake combusted with the fuel mixture. Sulphates and chlorides which are shown in Figure 31 and Figure 32 (points with P_2O_5<10 mol%) for both fuels bark and rapeseed cake were almost entirely found in particles with a high calcium content.

For rapeseed cake ash samples alkali metals were observed mainly together with phosphorus. The fact that alkali metals will primarily form phosphates was reported in literature[181]. In the bottom ash from test B0 (Figure 31 b) and B10 (Figure 32 b) mainly phosphate particles were found. Numbers 1, 2, and 3 in all ternary diagrams indicate different forms of phosphates. Number 1 indicates orthophosphates (PO_4^{3-}), with approximately 25 mol% of P_2O_5. Phosphorus can form other structures also like polymeric ions, such as metaphosphates ($P_3O_9^{3-}$) and pyrophosphates ($P_2O_7^{4-}$).[88] The formation of tripolyphosphates ($P_3O_{10}^{5-}$) in biomass ash samples was also reported[121]. Pyrophosphates

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point	Na$_2$O	MgO	P$_2$O$_5$	K$_2$O	CaO
1	6	6	33	26	30
2	12	2	31	20	35
3	20	3	28	12	38
4	14	3	30	17	36
5	9	12	30	21	28
6	7	7	33	25	28
7	13	12	29	20	26
8	5	46	28	22	0
9	18	6	27	14	35
10	9	2	31	21	37
11	3	13	33	27	24
12	4	3	32	25	36
13	5	43	31	21	0
14	9	7	33	28	22
15	2	3	35	29	32
16	23	4	25	6	42
17	4	48	27	21	0
18	4	48	27	22	0
19	26	4	25	6	39
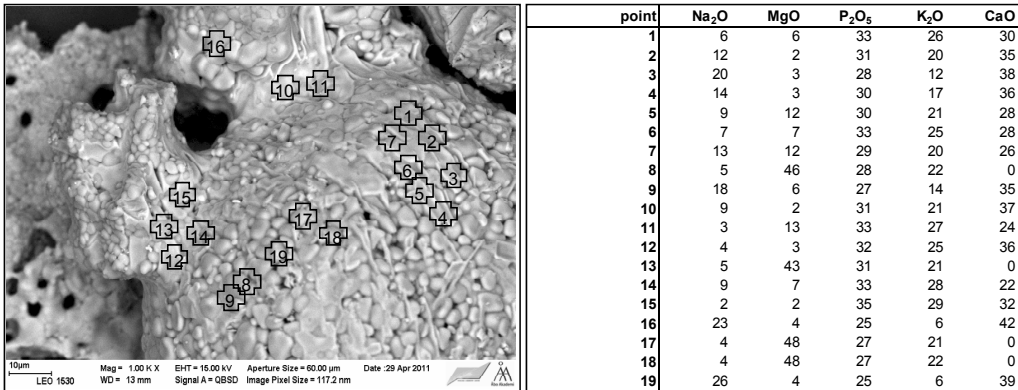
Figure 33 *Example of RC ash particle from the bottom ash sample after 8 hours of fluidized bed combustion at 800 °C and its composition on oxide basis as mol%, based on SEM\EDX studies. Composition normalized to 100 mol%. Before normalization, the composition ranged between 94 mol% to 100 mol% for the shown elements (Paper IV).*

and tripolyphosphates could be found in diagrams with approximately 33 mol% and 38 mol% of P$_2$O$_5$. This range of phosphorus content is indicated by number 2. On the other hand, the composition in number 2 could also correspond to mixtures of the different types of phosphates mentioned.

It is difficult therefore to state if group 2 indicates pure pyro- and tripoly-phosphates or denotes formation of phosphate mixtures. Number 3 corresponds to the formation of methaphosphates.

In Figure 33 an example of rapeseed cake ash particle from test B0 is shown. The particle shows a heterogeneous composition with high phosphorus content. It is plausible that different types of phosphates are present in one ash particle. Additionally, there seems to be a correlation in the forms of phosphates: K and Mg are found together in higher concentrations in the same points, and this also holds true for Na and Ca. Based on SEM/EDX analysis the formation of some compounds may be inferred. Figure 33 suggests that orthophosphates such as CaNaPO$_4$ (point 16) and MgKPO$_4$ (point 17 and point 18) are present together with other phosphates, e.g. with a composition close to that of CaK$_2$P$_2$O$_7$ (point 1). While such compounds were previously indentified in biomass ash samples[85] the sodium rich compounds have not been reported recently. The other point analyses in this particle indicate the presence of complex phosphate mixtures. The melting behaviour of
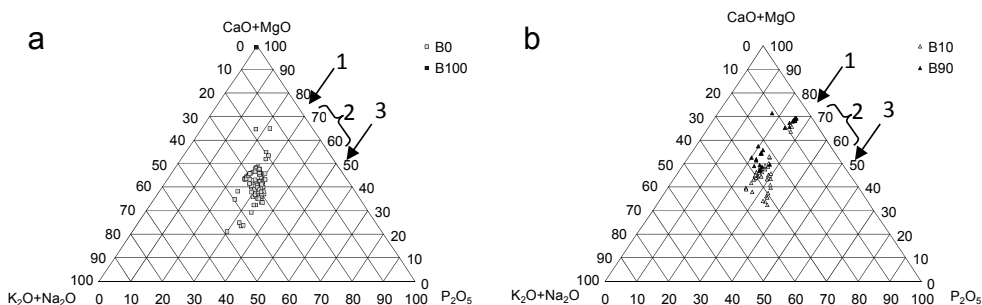
Figure 34 *Composition of ash particles in bottom ash samples from tests with 100% fuel (a), B0 and B100, and mixtures (b) with a high proportion of rapeseed cake (B10) and with high proportion of bark (B90) based on SEM/EDX. Composition normalized to 100%. Before normalization the sum of the oxides in the corners was above 90 mol% (Paper IV).*

mixtures can drastically differ from the melting behaviour of pure compounds, influencing the amount of melt present in and the first melting point of the ash. The substantial amount of sodium found in these mixtures may have a considerable influence on the melting behaviour of phosphates.

In order to determine the approximate amount of alkali and alkaline earth metals in the phosphate compounds, analyses of points with phosphorus as the main anion were chosen and shown in ternary diagrams (Figure 34 and Figure 35).

In Figure 34 it can be seen that phosphates formed during rapeseed cake combustion can contain as low as 20 mol% (CaO+MgO). The composition of ash particles, which is in the range 2 with P_2O_5 between 60-70 mol%, contains between 20-40 mol% of (CaO+MgO). For
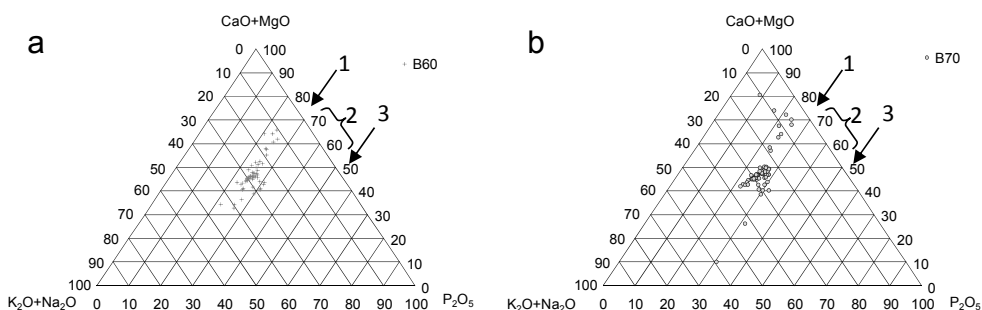
Figure 35 *Composition of ash particles in bottom ash sample for tests B60 (left) and B70 (right) based on SEM/EDX. Composition normalized to 100%. Before normalization the sum of the oxides in the corners was above 90 mol% (Paper IV).*

test B90, phosphates found in the bottom ash indicate orthophosphates (indicated with point 1) with an alkaline earth metals content at approximately 50 mol% and higher. This corresponds well with, e.g., $CaKPO_4$ previously being reported to form during biomass combustion.[85] This compound has a high melting temperature. Almost all point analyses from tests B60 and B70 (Figure 35) indicate orthophosphates formation. As indicated in Figure 30, the (K+Na)/(Ca+Mg) fuel molar ratio is decreasing with higher proportion of bark in the fuel mixture and is favouring formation of alkaline dominated phosphates (Figures 34 and 35).

4.2.4 Agglomeration characteristics (Paper III)

SEM/EDX analyses of cross-section of agglomerates formed after the agglomeration test (stage 2) are shown for 100 wt% rapeseed cake and 100 wt% bark in Figure 36. In the case of pure bark firing the composition of the neck formed between the two bed material grains resembled the composition of the inner reaction layer (*Paper III*). Therefore it is expected to be the reason of bed material sintering. A reaction between the silica bed material particles and the ash-forming elements originating from the fuel, which leads to layer formation, is the dominant mechanism underlying agglomerate formation. This

	weight-%	atom-%		weight-%	atom-%		weight-%	atom-%
P	29.9	30.4	P	30.4	30.6	P	30.6	31.8
Si	9.4	10.5	Si	13.1	14.5	Si	12.7	14.6
Al	0.0	0.0	Al	0.0	0.0	Al	0.0	0.0
Mg	4.3	5.6	Mg	15.7	20.2	Mg	7.4	9.8
Ca	27.2	21.4	Ca	7.2	5.6	Ca	15.4	12.4
Na	15.2	20.9	Na	4.1	5.6	Na	6.2	8.8
K	14.0	11.3	K	29.4	23.4	K	27.7	22.8
Mn	0.0	0.0	Mn	0.0	0.0	Mn	0.0	0.0

	weight-%	atom-%		weight-%	atom-%		weight-%	atom-%
P	0.6	0.6	P	6.8	6.9	P	0.0	0.0
Si	62.6	68.2	Si	48.6	54.0	Si	43.4	51.9
Al	0.2	0.3	Al	0.5	0.6	Al	0.0	0.0
Mg	1.0	1.3	Mg	0.7	0.9	Mg	0.5	0.7
Ca	10.3	7.9	Ca	18.6	14.5	Ca	50.7	42.5
Na	4.1	5.5	Na	6.2	8.4	Na	0.7	1.1
K	20.2	15.8	K	17.9	14.4	K	4.0	3.4
Mn	0.9	0.5	Mn	0.7	0.4	Mn	0.8	0.5

Figure 36 *Agglomerates found for the test with rapeseed cake (left) and bark (right) (Paper III).*

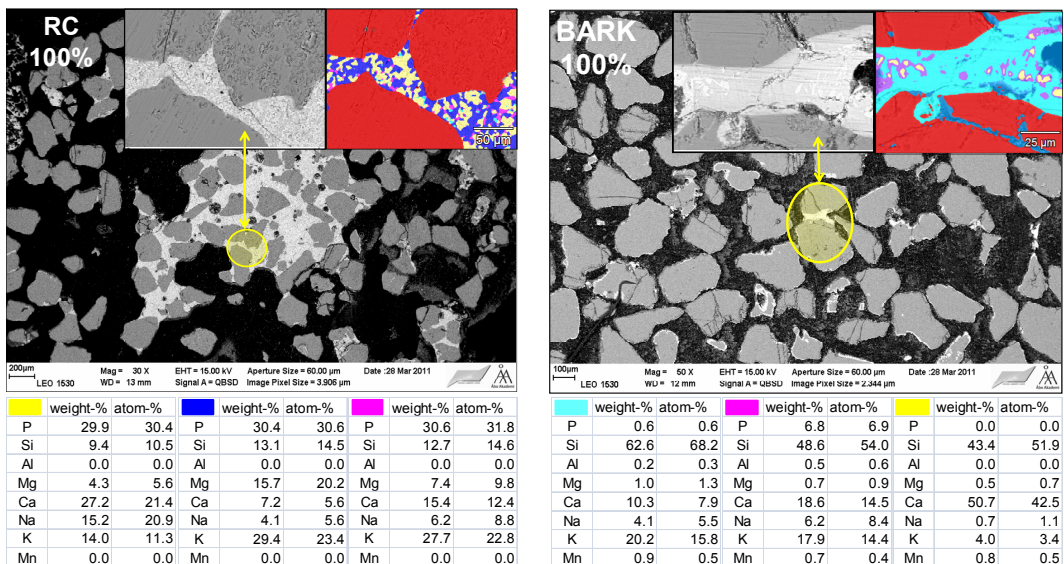mechanism can be described as a reactive mechanism. In the case of 100 wt% RC, the direct adhesion of partly molten ash particles to bed particles can be the driving force for the formation of agglomerates. Since no chemical interaction was observed between the bed material particles and the molten ash, this mechanism is referred to as a non-reactive mechanism. Both mechanisms are summarized in Figure 11.

In *Paper III* the distribution of the total layer thickness around the bed material particles was also studied in an attempt to define the prevailing mechanism of agglomeration for fuel mixtures. It was found that in mixtures containing at least 40 wt% bark, the non-reactive mechanism prevails. In mixtures containing at least 60 wt% bark, the reactive mechanism prevails. In the mixture with 50 wt% bark, there is evidence that both mechanisms may play a role in bed agglomeration.

Investigations of the agglomerate neck composition during the combustion of 100 wt% RC revealed that the partly molten ash found between the silica sand particles consisted mainly of phosphates: magnesium-potassium-phosphates, and calcium-potassium/sodium-phosphates. Because of the high sodium content of rapeseed cake, the combustion of 100 wt% RC results mainly in the formation of sodium-calcium-phosphates.

4.3 Co-firing in a semi-industrial CFB (Paper V-VI)

4.3.1 Elemental mass balance (Papers V-VI)

Elemental flows were calculated using the quantitative analyses of the incoming and outgoing streams. The results are shown in Figure 37 giving an indication of the pathways that ash-forming matter was taking throughout the boiler. The figure is divided into bottom ash, secondary cyclone ash, bag filter ash, and emission fractions of elemental inflow. The sum of those flows indicates the elemental mass balance closure (outflow/inflow [%]). The difference between the sum and 100% is marked on the graph as an accumulated ash fraction in the system; this naturally also includes any possible measurement errors. During the coal test without limestone the mass balance of calcium, sulphur, and chlorine exceeded 100%. Coal with limestone addition was fired prior to the test without limestone addition. When no limestone was added the cleaning of the boiler
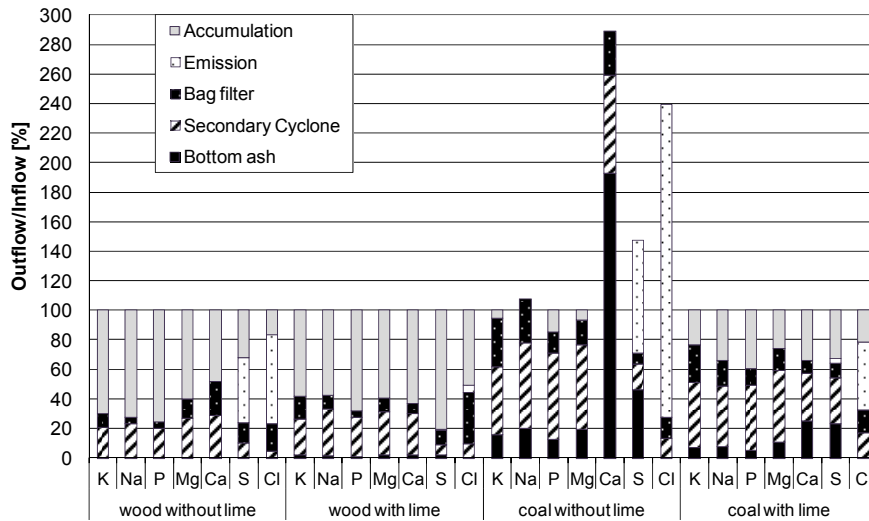
Figure 37 *Elemental mass balances shown as outflow/inflow of the element in [%].
Accumulation (or error) bar calculated as a difference of the mass balance closure
and 100% (Δ = 100 [%] - out/in [%]) (Papers V-VI).*

can be observed. This high concentration in bed material was a result of high bed
regeneration during this test and removal of calcium sulphate accumulated during the
limestone test.

The secondary cyclone stream was the main fly ash stream for both, wood and coal case.
During wood case, 20-25% (during coal, 40%) of entering alkali metals and phosphorus
were found in the secondary cyclone stream as particles >10 μm.

The total ash recovery for wood (*Paper V*) without limestone was approximately 70%
ash$_{out}$/ash$_{in}$, indicating ash accumulation in the system. This indicates possible
agglomeration and fouling tendencies occurring during RC co-combustion with woody
biomass. For coal (*Paper VI*) without limestone the closure was above 90% ash$_{out}$/ash$_{in}$
indicating no significant ash accumulation in the system. However, some ash accumulated
during this test and was removed from the boiler during the following coal combustion at
the end of the experiments resulting in mass balance closure higher than 100%.
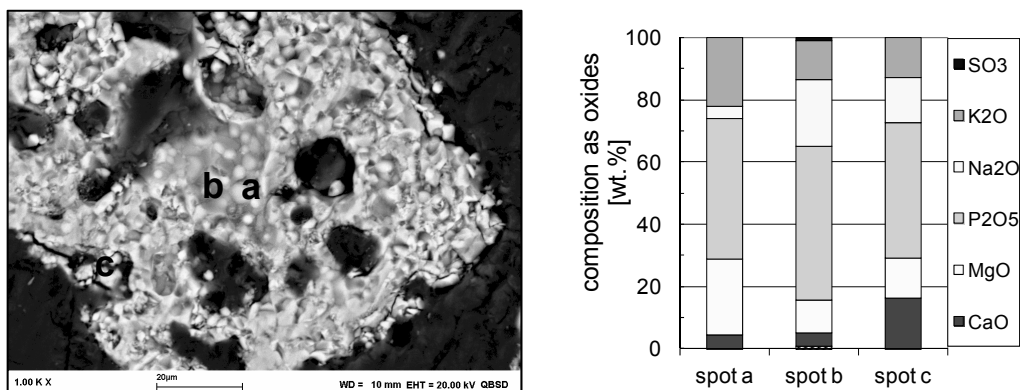
Figure 38 *Rapeseed cake ash particle found in the bottom ash after 12 hours of rapeseed cake and wood co-combustion.*

4.3.2   Agglomeration characteristics (Papers V-VI)

During combustion, rapeseed cake forms ash particles that are heterogeneous in their composition consisting of both alkali and earth alkaline metals (Figure 38). As discussed in previous sections the melting behaviour is changing with the content of alkaline earth metals (Figure 26). In *Paper III*, it was shown that RC ash particles could lead to defluidization already at 800 °C. In *Paper V*, during co-combustion of wood and a small proportion of rapeseed cake, a high agglomeration tendency was observed. The proportion of rapeseed cake (RC) during combustion of wood with and without limestone was approximately 15% on an energy basis. This fuel proportion results in a doubled RC ash inflow compared to wood ash inflow. The test without limestone addition led to the formation of agglomerates in the particle seal and the shutdown of the boiler occurred. On the other hand the test with limestone addition did not result in any drift problem.

Agglomeration during the test without limestone addition was attributed to the formation of low melting temperature K-silicates on the surface of the bed material grains and adhesion of phosphorus-rich, partly molten ash particles. The addition of limestone improved co-combustion. It prevented the formation of a low melting temperature reaction layer (K-silicate) on bed material particles by coating the grains with uniform calcium layer, as can be seen in Figure 39 (the white band around the grey silica core).
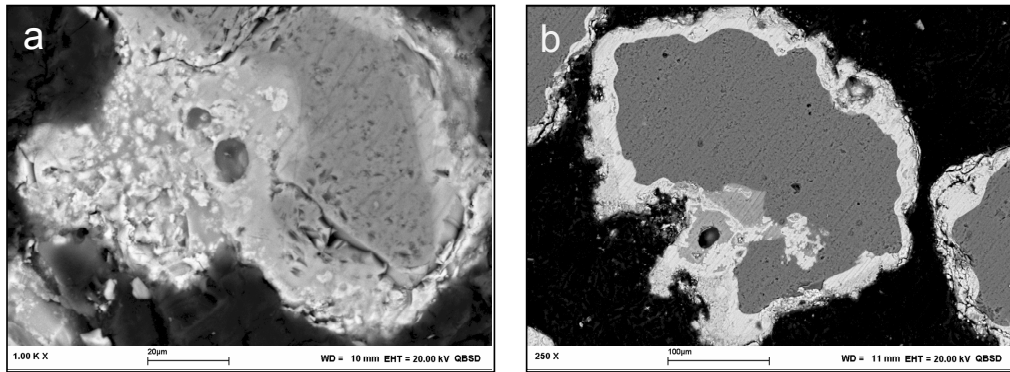
Figure 39 *Bed material grains after co-combustion of rapeseed cake with wood a) without limestone addition and b) with limestone addition (Paper V).*

During coal co-combustion no bed sintering was observed and the outer coating layer was dominated by coal ash. There could be two reasons for the observed weak agglomeration tendency. Coal ash might have acted as a diluting agent for low melting temperature RC ash particles (4-fold higher coal ash flow compared to RC ash inflow). However, also the influence of coal ash chemistry could be taken into consideration. Alkali released could have been scavenged in the bed by ash compounds originating from coal in the form of high melting temperature aluminium silicates. The interactions of phosphates with coal ash should be also considered. However, the reaction of phosphorus with aluminum silicates leading to the formation of high melting temperature compounds is not well understood yet and requires further investigation.

4.3.3 Fouling characteristics (Papers V-VI)

The measurements carried out in the beginning of the convective pass are shown in Figure 40. The increased formation of alkali metal chlorides during limestone addition for wood case took place (a). The increase in chlorides is followed by the increased rate of deposit build-up (RBU) on the deposit probe and creates the risk of corrosion. Correspondingly (K and Na) concentration in the bag filter fraction was raised and the chlorine content doubled compared to the no limestone test. This could be a result of calcium sulphate formation. When no sulphur was released to the gas phase the sulphation of (KCl+NaCl) was not possible[182]. The fact that limestone was found to

indirectly facilitate the formation of (K and Na)Cl during wood combustion was not observed during coal case (Figure 40 b). No alkali chlorides in the gas phase were formed but also no chlorine was found in the bag filter ash. This indicates a significant influence of aluminium silicates from coal ash on alkali metal compounds as was earlier reported in the literature[183].

The composition of deposits collected during the tests is shown in *Papers V* and *VI*. Here the composition of a leeward side deposit is shown in Figure 41 since there the highest concentration of phosphorus was observed.

a) Rapeseed cake and wood combustion
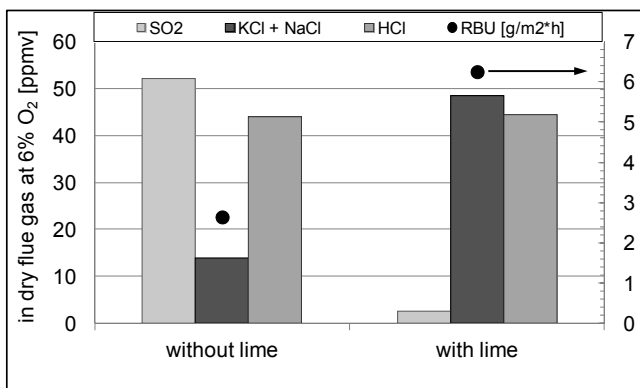
b) Rapeseed cake and coal combustion
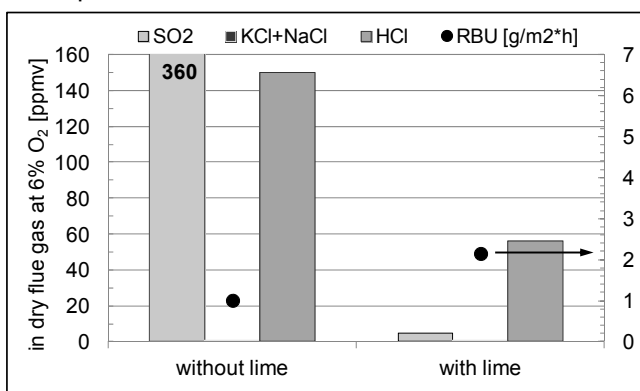
Figure 40 *Measurements at the entry to the convective pass (Papers V-VI).*

The increase of chlorine during wood and rapeseed cake co-combustion when limestone was added can be observed. This is a result of increased formation of (KCl+NaCl). High content of calcium in the deposit indicates limestone induced fouling. For the test with limestone addition a decrease of phosphorus concentration in the deposits can be observed. This was most probably the result of the favoured formation of calcium phosphates which most probably stayed in the bed. During the coal case no deposition of chlorides could be observed in the deposits both with and without limestone addition.

Figure 41 *Composition of leeward deposit based on SEM/EDX shown as wt% of oxides (Papers V-VI).*

Furthermore, when no limestone was added hardly any deposit was collected. This observation suggests that the rapeseed cake and coal mixture does not cause fouling.

In has been previously reported that ash-related problems could be counteracted when co-combusting biomass with coal.[184,185] It seems that ash-related problems during combustion of phosphorus-rich fuels can also be reduced during coal co-combustion.

4.4 Evaluation of characterization methods

Different laboratory methods were used in this study to determine the main challenges related to the residues combustion. They served their purpose well but certainly each of them has some disadvantages. Therefore they should be used with caution when interpreted in terms of full-scale applications.

Development of an analytical method was not the objective of this research. However, when applying them to answer the research questions; several sources of uncertainties

were observed. The main uncertainties of the methods could arise from accuracy of the instruments, measurement conditions, operator effects, and sampling. These can be, of course, minimized with the calibration of the instruments, good control of the measurement conditions, and the precise and systematic way of carrying out the experiments. It is also of great importance to eliminate the human factor during the process of data evaluation. Methods mostly influenced by this uncertainty are the two sintering methods: microsample and standard ash sintering methods. For the last one a MATLAB routine was used in order to avoid subjectivity. The largest challenge for all of these methods comes, however, with sampling. Samples used for analysis with all methods were in the range of grams to nanograms and were supposed to be representative for the bulk material measured in tonnes. Therefore, the representativeness of the sample is of crucial importance for all of the methods. In this work two main measures were applied in order to minimize uncertainties originating from sampling: homogenization and repetition. However, this uncertainty should be kept in mind when carrying out analyses.

An initial estimation of fuel properties is given with the standard fuel analysis, which can be used as a starting point. This is relatively easy to carry out. It shows only fuel composition and heating values with no indication of process behaviour. Chemical fractionation gives additional information on ash-forming matter, which could be then interpreted in terms of the elements' reactivity. However, this correlation is not always straightforward and is recently more discussed in terms of elements than in terms of leached fractions. In this study the method was used not to predict the ash behaviour but to show the way ash-forming matter is present in a fuel and to fulfil other methods with this information. In *Paper II* three different laboratory-scale sintering tests were used and results were compared in order to determine the sintering tendency of the residues. One important parameter of these methods to bear in mind is that two of them (the pellet sintering test and the standard sintering test) are performed on ash. In this study ash samples were prepared at 550 °C (standard ash). This does not correspond to ash formed during full-scale combustion and therefore they do not give the process temperature.

These could be used, however, to study fuel ash properties and for conducting comparative studies. On the other hand, microsample sintering tests were performed on fuel samples eliminating ashing temperature as a limiting parameter. However, since the results are based on microscopic visual inspection, they might be somewhat subjective. Another drawback of all sintering tests (*Paper II*), is that neither of them recognizes the influence of bed material nor the fluidization velocity. Even though they give valuable information on sintering tendency, they cannot be directly correlated with the bed sintering tendency of a fluidized bed.

Agglomeration tests were performed in a bench-scale BFB (*Paper III-IV*). The combustion stage with the continuous feeding and combustion at temperatures relevant to fluidized bed operating conditions can be directly correlated to a full-scale operation, and therefore the accumulated ash should show the same properties. On the other hand, the agglomeration stage cannot be directly correlated with the real process due to the constant heating rate and the none combustion of fuel particles in the bed during the measurement. It indicates the initial bed sintering temperature, taking account of bed material and fluidization velocity. Semi-industrial scale experiments (*Paper V-VI*) give the best indication of the combustion behaviour of tested residues. However, the number of scale-up experiments will be limited due to the operation being costly and time-demanding. Both laboratory and bench-scale studies could provide useful information on the combustion behaviour and therefore should proceed full-scale testing.

5 CONCLUSIONS

Extensive fuel characterization was undertaken and proved that the residues could be a valuable source of heat and power. The residues differ substantially in their composition compared to more traditional biomass fuels. A common property is the high concentration of phosphorus. This element was considered until now as negligible for ash chemistry due to its low concentrations in fuels. The experimental work revealed that phosphorus has a role during combustion which cannot be neglected anymore when phosphorus-rich fuels are entering the energy market.

Agricultural residues and wastes contain a high concentration of phosphorus which has a crucial effect on ash sintering. Laboratory-scale (*Papers I-II*) investigation defined the challenges related to the combustion of the investigated residues. Relatively low ash sintering temperatures (*Paper II*) were observed for phosphorus-rich fuels when present together with a high content of soluble alkali metals. It was observed that the higher the content of alkaline earth metals in the ash samples, the higher was the sintering temperature. This was confirmed during bench-scale studies in *Papers III-IV* and semi-industrial scale studies in *Papers V-VI*.

Limitations of combustor availability associated with silica bed sintering and deposit formation of phosphorus-rich fuel were studied on the sample of rapeseed cake. This fuel next to phosphorus contains high concentration of potassium and also sodium. High agglomeration and fouling tendency during fluidized bed combustion was observed. In order to improve the problematic behaviour two strategies were used: co-combustion and the addition of limestone.

Bed sintering during fluidized bed combustion of pure rapeseed cake followed non-reactive mechanism. This mechanism is controlled by the stickiness of fuel-derived ash particles. Entrained fine rapeseed cake ash particles also aggravated the deposit formation. During co-combustion experiments of rapeseed cake with wood, deposit mainly built up on the windward side of the deposit probe. However, the highest concentration of phosphorus was found on the leeward side.

Co-combustion of rapeseed cake with bark proved to decrease agglomeration tendency of phosphorus-rich fuel. With an increasing proportion of bark, Ca/P increased in the fuel mixture and the formation of high melting temperature phosphates in the ash was favoured. However, bark addition also favoured the formation of low melting temperature K-rich reaction layer on the silica bed material grains. Increasing Ca/P ratio to 1.3 resulted in a significant decrease of the agglomeration tendency when the (K+Na)/(Ca+Mg) molar ratio was approximately 0.8.

During co-combustion of rapeseed cake with wood, the addition of limestone resulted in improved combustion and no heavy bed sintering was observed, even though the retention of phosphorus in the bed took place. Limestone addition was used to favour the formation of high melting temperature phosphates during rapeseed cake and wood co-combustion tests. Additionally, limestone also induced coating of bed material grains with a thick and uniform calcium dominated layer which prevented reaction of potassium with silica from the bed. The amount of phosphorus in the leeward side deposit was decreased with limestone addition; however, at the same time the formation of (KCl+NaCl) was increased.

During rapeseed cake co-combustion with coal, neither bed sintering nor fouling was observed. The ratio of coal ash inflow to rapeseed cake ash inflow was four times higher thereby diluting the low melting temperature rapeseed cake ash particles, but the interaction of aluminium silicates with rapeseed cake ash may also take place.

6 FUTURE WORK

The combustion characterization of phosphorus-rich fuels was investigated, indicating possible challenges and possible countermeasures. There is still a need, however, for more fundamental studies on phosphorus. Detailed reaction mechanisms behind bed agglomeration and fouling should be further investigated. The interactions of phosphates with silica and aluminum silicates were not investigated in this study, and require better understanding.

This work proved that co-combustion with bark reduced the agglomeration tendency of phosphorus-rich fuels. However an examination of the influence on deposit formation was not undertaken. Before the full-scale implementation the fouling tendency during rapeseed cake and bark co-combustion experiments should be investigated as well as the long term effect on the combustor operation.

Understanding thermodynamic properties of compounds formed during biomass combustion is an important step for ash behaviour determination. Thermodynamic data for phosphates are, however, scarce. The determination of thermodynamic properties of phosphorus compounds is, therefore, crucial for a better understanding of ash chemistry during combustion of phosphorus-rich biomass.

Another aspect for future studies is ash utilization. As was demonstrated, ash from combustion of the residues could be rich in phosphorus. Consequently its potential use as fertilizer on agricultural land should be further studied. It would close the cycle of phosphorus and could add extra value to the production process from which the residues were obtained.

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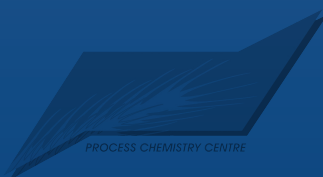
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