



Final Report 2007-2010

Nordic Graduate School of
Biofuel Science and Technology

BiofuelsGS-2

Chalmers University of Technology, Sweden

Technical University of Denmark, Denmark

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Preface

The Nordic Graduate School in Biofuels Science and Technology – Phase 2 (BiofuelsGS2) is a postgraduate programme operated jointly by the four universities Chalmers University of Technology (CTU), Sweden, Technical University of Denmark (DTU), Denmark, Norwegian University of Science and Technology (NTNU), Norway, and Åbo Akademi University (ÅAU), Finland.

BiofuelsGS2 is a direct continuation to the former Nordic graduate school “biofuelsGS”, which was established in 2003. BiofuelsGS2 is funded by the Nordic Energy Research for the period of four years, starting the 1st of January 2007, ending the 31st of December 2010.

The members of the schoolboard are Professors Bo Leckner (CTU), Kim Dam-Johansen (DTU), Johan Hustad (NTNU) and Mikko Hupa (AAU), who is also acting as chairman. The coordination of the graduate school was led by Doc. Bengt-Johan Skrifvars (AAU) until October 2007 when Dr. Tech. Maria Zevenhoven (AAU) took over. The coordination office is located at Åbo Akademi University in Turku, Finland.

A team of senior researchers is tightly cooperating with the coordination to organize the program planned to be performed in BiofuelsGS-2. The team consists of Prof. Peter Glarborg, Dr. Flemming Frandsen, Dr. Jytte Boll Illerup, (DTU), Dr. Henrik Thunman, Dr. Lars-Erik Åmand (CTU), Dr. Øyvind Skreiberg, Dr Morten Grønli (NTNU) and Dr. Anders Brink (AAU).

This BiofuelsGS2 final report reviews the activities as taken place in the school from 2007-2010. During this period students have reported their progress yearly.

Furthermore, the report provides general information about the BiofuelsGS-2 as well as of the participating universities.

About BiofuelsGS2

The goal of the new Graduate School, the BiofuelsGS-2, is to continue to raise the esteem and quality of the doctoral training within the Nordic universities in the area of biomass and waste conversion to fuels, heat and power. The graduate school aims also at providing the basic scientific and technical knowledge to solve problems related to conversion of biofuels. This is achieved by collaboration in postgraduate course arrangements, shared student supervision by student and supervisor visits between the base universities, and intensive industry-academia networking.

The BiofuelsGS2 consists of 16 students (partly funded directly by the school, partly funded by other sources) and their supervisors. Also, additional students from the four partners are given the possibility to participate with funding from other sources.

The individual courses of biofuelsGS-2 are advertised broadly and are open to students at all participating Nordic universities.

In summary, the School activities include:

- Tailor-made study and research plans for all participating students, including study and research visits at other Nordic universities.
- Intensive courses organized directly by the school: In key topics of biofuel conversion science and technology, provided by the senior researchers and professors within the participating universities or by invited lecturers from industry.
- Intensive courses organized by others: Additional courses were provided by cooperating partners to BiofuelsGS2 such as the Danish Graduate School of Chemical Engineering, "Molecular Product and Process Technology (MP2T)", the Finnish Graduate School in Chemical Engineering (GSCE) and the Swedish postgraduate training program CeCost.
- Annual seminars where the students present their work and discuss with each other.
- An Annual Book published at the annual seminars, consisting of progress reports by the students of the School.
- A website <http://web.abo.fi/instut/biofuelsGS-2/>

Activities 2007-2010

The BiofuelsGS2 was initiated the 1st of January 2007. At the moment of writing the school counted 16 participating students. Information was spread through the website of BiofuelsGS2 and a biannual newsletter sent to participants and their supervisors. Through the website information about the program such as courses, meetings and seminars is delivered. The site also provides a description of the school and a list of contact addresses of all participants.

Two courses were held during the fall of 2007. The first was held in Turku, Finland at Åbo Akademi University the 22nd - 26th of October; "Chemistry in combustion processes part II".

The second was held in Gothenburg at Chalmers University of Technology the 19th - 23rd of November, "Thermal conversion of solid biomass and wastes".

In 2007 three students from the earlier BiofuelsGS and from this present school have achieved their academic goals.

From CTH, David Pallarès, has defended his doctoral thesis within the subject; Fluidized bed combustion modeling and mixing.

From AAU, Daniel Lindberg, has defended his doctoral thesis within the subject; Thermochemistry and melting properties of inorganic alkali compounds in black liquor conversion processes.

From DTU, Niels Bech, has defended his doctoral thesis within the subject; In situ flash pyrolysis of straw. From NTNU, Michaël Becidan, has defended his doctoral thesis within the subject; MSW/ Biomass devolatilisation/pyrolysis with emphasis on NOx precursors, product distribution, gas composition and weight loss.

One student took the opportunity to visit a partner laboratory. Sven Hermansson (CTH) spent three months in Åbo Akademi in the autumn of 2007.

In 2007 the annual seminar was held in Kimito in Finland with AAU as host.

During 2008 two students from Åbo Akademi finalized their licentiate theses with the following topics; Tor Laurén: Methods and Instruments for Characterizing Deposit Buildup on Heat Exchangers in Combustion Plants and Micaela WesténKarlsson; Assessment of a Laboratory Method for Studying High Temperature Corrosion Caused by Alkali Salts.

In 2008 this seminar was held in Visby on 14th - 16th of September. CTH acted as host for the seminar.

In 2008 the graduate school started its largest effort, i.e. a course in 4 parts on "Analytical Techniques In Combustion" was organized. This course aims to give students a critical view on analytical tools available for studying combustion processes.

Part 1 of the Nordic course was held at CTH in October 2008. Students were able to join a measurement campaign and were introduced in the secrets of online analyses and solid sampling. During the campaign wood and straw were co-fired and different techniques were used to minimize alkali chloride formation. The measurement campaign formed a red thread through the other 3 parts of the course.

Part 2 of the Nordic course was held at DTU in February 2009 and the third held at NTNU in May 2009. The last part took place at AAU in September 2009. Samples taken during the campaign were analysed with analytical techniques available and combustion experiments were carried out in lab scale facilities.

After the course all groups of students wrote a scientific report on different subjects encountered during the course such as "Mass and specie balances", "Fuel nitrogen conversion in the CFB", "Fuel nitrogen conversion in oxyfuel combustion", "Deposit formation", "Influence of the addition of straw and ammonium sulphate on bed material and fly ash composition", etc. Summaries of results are presented in this report as well

During 2009 Daniel Stanghelle, Robert Johansson and Kim Hougaard Pedersen defended their doctoral theses. Liang Wang (NTNU) spend almost a month at DTU.

The annual seminar was held near Trondheim

2010 was the last year of GS Biofuels 2.

During this year AAU organized its yearly courses Chemistry in Combustion 1 and 2 and Sven Hermansson and Markus Engblom defended their thesis.

Finland was host for the International Conference on Impact of Fuel Quality on Power Production and the Environment in Saariselkä and we were happy that we had a representation of the school's students there, i.e. Wu Hao, Muhammad Shafique Basir and Liang Wang.

The last seminar was held in the centre of Copenhagen.

2007-2010

Participating universities:

Åbo Akademi University (AAU), Finland Process Chemistry Centre

The Process Chemistry Centre at Åbo Akademi (PCC) is a research centre active in the field of chemical engineering. It has four major focus areas of which one is combustion and materials chemistry research. The PCC was granted the status of "Center of Excellence" by the Academy of Finland the first time in the year 2000 and has renewed this status in 2006. The status of "Center of Excellence" will continue until 2011.

The PCC studies physicochemical processes at the molecular level in environments of industrial importance, in order to meet the needs of tomorrow's process and product development. This mission statement is realized in the combustion and materials chemistry research in two subdivided themes:

- Combustion
 - Modelling
 - Experimental
- Materials
 - Biomaterials
 - Conventional

Åbo Akademi University has been active in the area of combustion and materials chemistry since 1974. Work performed has included both basic research and troubleshooting cases.

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Chalmers University of Technology (CTU), Sweden Department of Energy and Environment

The department consists of several sections, among them a research group dealing with energy conversion. The research group which is of interest for the present activity, the division of Energy Conversion, works with combustion devices and conversion (drying, devolatilization, combustion and gasification) of solid fuels, biofuels and wastes with respect to efficiency, reliability and environmental performance. The combustion technologies of primary interest are fixed and fluidized bed. The department operates one of the largest research plants available in Europe (in the world, except China), a 12MWth circulating fluidized bed boiler.

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Technical University of Denmark (DTU), Denmark, Combustion and Harmful Emission Control (CHEC) Research Center

The CHEC (Combustion and Harmful Emission Control) Research Centre, at the Department of Chemical Engineering of the Technical University of Denmark, carries out research in fields related to chemical reaction engineering and combustion, focusing on high temperature processes, formation and control of harmful emissions, and particle technology. CHEC has achieved international recognition through a combination of experimental techniques and modelling. Laboratory experiments provide detailed and accurate data on chemical and physical processes in the systems studied. The data is subsequently interpreted by mathematical modeling based on chemical kinetics, chemical reaction engineering, multiphase and component thermodynamics, and fluid dynamics.

The CHEC laboratories are well equipped and include equipment for gas adsorption and mercury porosimetry, particle size distribution, simultaneous thermogravimetric and differential scanning calorimetric, Fourier transform IR, high temperature light microscopy, and ash viscosity measurements. The laboratories also include a lab scale wet flue gas desulphurization column, a SCR testrig, and a number of reactors from lab to pilotscale, used to characterize and investigate fixed bed, entrained flow and fluid bed combustion processes, emissions, ash formation, deposition and corrosion.

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Norwegian University of Science and Technology (NTNU Norway) Department of Energy and Process Engineering

The Department of Energy and Process Engineering has a total of 150 employees, including approximately 80 PhD students. We have an extensive contact net, and our Master students are employed by both industry and public administration. Research is applied by offshore and onshore industry, by consulting companies, for energy advisory services, by engineering companies and public administration.

The Department of Energy and Process Engineering at the Norwegian University of Science and Technology is an international knowhow organization. The Department aims at being a driving force within education and research comprising the total energy chain from electricity/heat production to enduses in industry and buildings. Our activities include systems based both on natural gas and renewable energy. Pollution problems connected to the general environment and to the indoor/residential environment is an important part of this work. We also perform research on industrial process technology in a wider sense, including refining of Norwegian raw materials into superior and competitive products.

The aim of the department is to develop and communicate knowledge, thus contributing to added value and improvement of society. Our target is to be a premise provider to the authorities and an innovation resource unit for the Norwegian industry within our fields of science. By ensuring that Norwegian industry and the public authorities have access to knowledge of a high international level, we contribute to the solution of important issues in the society.

The Department has four specialist groups:

- Thermal Energy
- Industrial Process Technology
- Energy and Indoor Environment
- Fluids Engineering

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Organisation of BiofuelsGS2

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I am Professor in Inorganic Chemistry at the Åbo Akademi Process Chemistry Centre. My team's research activities deal with detailed laboratory studies and advanced modeling of the chemical aspects in various types of combustion systems, such as fluidized bed boilers, pulping industry spent liquor recovery boilers etc. I also have an interest in ceramic materials for various applications. Since 2006 I am also the Dean of our Technical Faculty at Åbo Akademi.



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I am professor in energy conversion technology at Chalmers University of Technology. I have mostly been working with questions related to combustion of solid fuels, combustion devices, and a number of different subjects ranging from reduction of emissions to heat and mass transfer. Much work has been connected to fluidized bed combustion.



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- High-temperature processes
- The formation and control of harmful emissions
- Particle technology
- Chemical product design



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My main research area is thermal conversion of solid, fluid and gaseous fuels to heat and electricity with focus on energy, economy, safety and the environment:

- Combustion and gasification technologies for biomass fuels and solid refuse-derived fuels in several different types of equipments.
- Combustion in diffusion flames, diluted flames, partially premixed flames and premixed combustion for boilers, Stirling Engines, gas turbines and in burners for off-gases from fuel cells (mainly catalytic burners).
- Fluidized bed technology
- Gas cleaning equipment
- Formation mechanisms for different pollutants in combustion
- Prediction, modelling and reduction of pollutants from several combustion technology processes both for land-based and off-shore plants and equipment.

Coordination



Associate Professor (docent)

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I am an associate professor (docent) in inorganic chemistry in combustion processes at the Åbo Akademi Process Chemistry Centre. My main research activities deal with:

- Ash behaviour and corrosion in energy conversion systems
- Recovery boiler chemistry
- Trace elements emissions

I am also involved in teaching at the university and have the executing responsibility of the basic chemistry course given for all students doing chemistry related studies at the university.



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TOPIC	Ash forming matter
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Besides acting as coordinator for the Nordic Graduate School of Biofuel Science and Technology, Biofuels 2, I am senior researcher in ash forming matter at the Åbo Akademi Process Chemistry Centre.

I wrote my PhD thesis on ash forming matter in biomass fuels in 2001 and since then I have been involved in different projects where ash forming matter, ash or heavy metals played an important role.

I am also involved in teaching at the university and coordinate the course Chemistry in Combustion processes-2



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Parallel to my studies in analytical chemistry at the Åbo Akademi University I worked in several projects connected to environmental analysis. After some years of laboratory work in the industry, because of some health problems and the fact that I wanted to have shorter workdays when my children started school, I found my way back to Åbo Akademi. Today I take part in the administration of the laboratory of analytical chemistry and work as a coordination assistant in three ongoing international projects at the Åbo Akademi Process Chemistry Centre

List of theses finalised during 2007-2010 (alumni from Biofuels GS included)

CTH:

Hermansson Sven, Detecting, Modelling and Measuring Disturbances in Fixed-bed Combustion, 2010 Doctoral thesis

Pallares David, Fluidized bed combustion - modeling and mixing, 2008 Doctoral thesis

Hermansson Sven, Disturbances in Fixed-Bed Combustion, Thesis for Degree of Licentiate of Engineering, Chalmers University of Technology, Göteborg, Sweden, 2007

AAU:

Engblom Markus, Modeling and Field Observations of Char Bed Processes in Black Liquor Recovery Boilers, 2010 Doctoral thesis

Laurén Tor, Methods and instruments for characterizing deposit buildup on heat exchangers in combustion plants, 2009 Licentiate thesis

Lindberg Daniel, Thermochemistry and melting properties of alcali salt mixtures in black liquor conversion proces, 2007 Doctoral thesis

Westén-Karlsson Micaela, Assessment of a laboratory method for studying high temperature corrosion caused by alkali salts, 2008 Licentiate thesis

DTU:

Kim Hougaard Pedersen Kim, Application of FlyAsh from Solid Fuel Combustion in Concrete, 2008 Doctoral thesis

Niels Bech Niels, In Situ Flash Pyrolysis of Straw, 2008 Doctoral thesis

NTNU:

Becidan Michael, Experimental Studies on Municipal Solid waste and Biomass Pyrolysis, 2007 Doctoral thesis

Khalil Roger, Thermal conversion of biomass with emphasis on product distribution, reaction kinetics and sulfur abatement, 2009 Doctoral thesis

Stanghelle Daniel, High temperature filtration of biomass combustion and gasification process, 2008 Doctoral thesis

List of publications of students: 2007-2010

Refereed articles of students

Andersson, K., Johansson, R., Hjærtstam, S., Johnsson, F., Leckner, B. *Radiation intensity of lignite-fired oxy-fuel flames*, Experimental Thermal and Fluid Science, 33(1), 67-76, 2008

Bergroth, N., Engblom, M., Mueller, C., Hupa, M., *CFD-based modeling of kraft char beds – part 1: char bed burning model*, Tappi J. 9(2), 6-13, 2010

Brink, A., Engblom, M., Hupa, M., *Nitrogen oxide emission formation in a black liquor boiler*, Tappi J. 7(11), 28-32, 2008

Bruun, E.,W., Hauggaard-Nielsen, H., Ibrahim,N., Egsgaard, H., Ambus, P., Jensen, P., Dam-Johansen, K., *Influence of fast pyrolysis temperature on biochar labile fraction and carbon sequestration*, Submitted for publication, 2010

Bäfver; L. S., Rönnbäck, M., Leckner, B., Claesson, F., Tullin, C., *Particle emission from combustion of oat grain and its potential reduction by addition of limestone or kaolin*, Fuel Processing Technology, 90, 353–359, 2009

Engblom, M., Bergroth, N., Mueller, C., Jones, A., Brink, A., Hupa, M., *CFD-based modeling of kraft char beds – part 2: a study on the effects of droplet size and bed shape on bed processes*, Tappi J. 9(2), 15-20, 2010

Engblom, M., Rönnqvist, A., Brink, A., Mueller, C., Jones, A., Hupa, M., *Recovery Boiler Char Bed Dynamics – Measurements and Modeling*, International Chemical Recovery Conference Proceedings, 1, 119-133, Tappi Press, 2010

Engblom, M., Mueller, C., Brink, A., Hupa, M., Jones, A. *Toward predicting the char bed shape in kraft recovery boilers*, Tappi J. 7(10), 12-16, 2008.

Engblom, M., Brink, A., Mueller, C., Hupa, M., Jones, A., *Reactive Boundary Layers in Kraft Char Bed Burning – Part 1: Mathematical Model*, submitted for publication

Engblom, M., Brink, A., Mueller, C., Hupa, M., Jones, A., *Reactive Boundary Layers in Kraft Char Bed Burning – Part 2: Model Predictions Vs. Experimental Results*, submitted for publication

Filbakk, T., Skjevraak, G., Dibdiakova, J., Jirjis, R., Høibø, O., *The influence of storage and drying methods for Scots pine raw material on mechanical*

pellet properties and production parameters, Submitted to Fuel Processing Technology

Hermansson, S., Thunman, H., *Two-dimensional CFD-modeling of multi-particle scale phenomena in fixed bed combustion*, To be submitted

Hermansson, S., Thunman, H., *Grate design and operational measures to reduce grate-material wear in fixed-bed combustion*, To be submitted

Hermansson, S., Lind, F., Åmand, L.-E., Thunman, H., *On-line monitoring of the fuel moisture-content in biomass-fired furnaces by measuring the relative humidity of the flue gases*, To be submitted

Hermansson, S., Lind, F., Åmand, L.-E., Thunman, H., *On-line monitoring of fuel moisture-content in biomass furnaces by measuring relative humidity of the flue gases*, To be submitted

Hjærtstam, S., Andersson, K., Johnsson, F., *Combustion characteristics of lignite-fired oxy-fuel flames*, Fuel, 88, 2216-2224, 2009

Hjærtstam, S., Normann, F., Andersson, K., Johnsson, F., *Performance of global reaction mechanisms in oxy-fuel conditions*, To be submitted

Hjærtstam, S., Johansson, R., Andersson, K., Johnsson, F., *Evaluation of gas radiation modeling in oxy-fired furnaces*, To be submitted

Ibrahim, N., Bech, N., Jensen, P. A., and Dam-Johansen, K., *Influence of water content on wheat straw pyrolysis*, Submitted for publication, 2010
Frigerio, S., Thunman, H., Leckner, B., Hermansson, S., *Estimation of gas phase mixing in packed beds*, Combustion and Flame, 153, 137-148, 2007

Lind, F., Seemann, M., Thunman, H., *A dual fluidised bed reactor for continuous catalytic tar reforming and catalyst regeneration*. To be submitted

Lindholm, J., Brink, A., Hupa M., *Flame retarding effects of some inorganic compounds in polyurethane adhesive*, To be submitted

Lindholm, J., Brink, A., Hupa M., *Influence of decreased sample size on cone calorimeter results*, Fire and Materials, to be submitted

Olsson, J., Pallarès, D., Johnsson, F., *Lateral solids mixing in a large-scale fluidized bed*. To be submitted

Skjevraak, G., Dibdiakova, J., Jirjis, R., Høibø O., *Changes in the chemical composition of wood material during pellets production and storage and drying of the raw material*. To be submitted

Skjevrak, G., Wang, L., *G Hydrolysis residue; properties of pelletized fuel in mixture with stemwood of Pine*, To be submitted.

Skjevrak, G., Wang, L., *Mixture of sintering reducing additives in pellets; mechanical fuel properties and combustion tests*, To be submitted

Sopha, B., Klöckner, C., Skjevrak, G., Hertwich E., *Norwegian households' perception of wood pellet stove compared to air-to-air heat pump and electric heating*, *Energy Policy*, 38(7), 3744-3754, 2010

Wu, H., Pedersen, A.J., Glarborg, P., Frandsen, F.J., Dam-Johansen, K., Sander, B., *Formation of fine particles in co-combustion of coal and solid recovered fuel in a pulverized coal-fired power station*, *Proceedings of the Combustion Institute*, 33, 2010 (in press)

Non-refereed articles from students

Andersson, S., Blomqvist, E., Bäfver, L., Claesson, F., Davidsson, K., Froitzheim, J., Karlsson, M., Pettersson, J., Steenari, B-M., *Minskad pannkorrosion med svavelrecirkulation*, Waste Refinery-rapport, WR-07, SWE, 2010

Aubert, M., Lindholm, J., Pawelec, W., Tirri, T., Amiri, R., N., Brink, A., Hupa, M., Wilén C.-E., *Design of novel non-halogenated flame retardants – combustion and polymer scientists join forces*, KETJU Annual Seminar, Helsingfors, Finland, 2010

Bashir, M. S., Jensen, P. A., Frandsen, F., Wedel, S., Wolfe, T., Dam-Johansen, K., Pedersen S. T., Wadenbäck, J., OA5.1, 18th European Biomass Conference, , Lyon, France, 03-07 May, 2010

Bashir, M. S., Jensen, P. A., Frandsen, F., Wedel, S., Dam-Johansen, K., Pedersen, S. T., Wadenbäck, J., *Impact of Fuel Quality on Power Production and the Environment*, Ivalo, Finland, 29-03 September, 2010

Bashir, M. S., Jensen, P. A., Frandsen, F., Wedel, S., Dam-Johansen, K., Wolfe, T., Pedersen, S. T., Wadenbäck, J., *Dansk Kemiingeniør Konference - DK2*, Lyngby, Denmark, 16-17 June, 2010

Brink, A., Karlström, O., Hupa, M., *A simplified model for the behaviour of large biomass particles in the splashing zone of a bubbling bed*, 20th International Conference on Fluidized Bed Combustion, Xi'an, China 18-20.5.2009

Claesson, F., Blomqvist, E., *Optimerad avfallshantering i Viareds Företagsförening*, Energiteknik, SP Rapport 2009:06, SWE, 2009

Claesson, F., Wikström Blomqvist, E., Johansson, A., Skrifvars, B-J., Andersson, B-Å., *Annual Variation In Elemental, Dioxin And PCB Content Within Swedish Waste Fuels – Results From Two Plants*, Published in the proceedings and presented at the 12th International Waste Management and Landfill Symposium, , Sardinia, Italy, October 5-9, 2009

Claesson, F., Skrifvars, B-J., Elled, A-L., Johansson, A., *Chemical characterization of waste fuel for Fluidized bed combustion*, Published in the proceedings and presented at the 20th International Conference on Fluidized Bed Combustion, Xi'an, China, May 18-20, 2009

Claesson, F., Johansson, L., Rönnbäck, M., Johansson, M., Tullin, C., *Particle emissions from combustion of oat grain with additives*, Published in the proceedings and presented at the 4th Biennial Meeting of the Scandinavian-Nordic Section of the Combustion Institute, Åbo/Turku, Finland, November 5-6, 2007

Engblom, M., Brink, A., Mueller, C., Hupa, M., *CFD-based modeling of laboratory scale kraft char bed burning*, 8th European Conference on Industrial Furnaces and Boilers (INFUB-8), Portugal, 25-28 March, 2008

Engblom, M., Brink, A., Mueller, C., Hupa, M., *CFD modellering av sodapannor vid Åbo Akademi*, Sodahuskonferens, Stockholm, 13 November, 2008

Engblom, M., Brink, A., *Influence of Stefan flow and boundary layer reactions on surface reaction rate*, Nordic Section of the Combustion Institute - Biennial Meeting, Åbo, 2007

Frandsen, F.J., Pedersen, A.J., Wu, H., Glarborg, P., Jensen, P. A., Madsen, O.H., Lundtorp, K., Sander, B., *Danish experiences on waste incineration on grates vs. coal-SRF co-firing in suspension*, 34th International Technical Conference on Clean Coal & Fuel Systems, Florida, USA, 2009

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Courses held during 2007-2010

Chemistry in Combustion 1 (2007)

Chemistry in Combustion 1 (2008)

Chemistry in Combustion 1 (2009)

Chemistry in Combustion 1 (2010)

Chemistry in Combustion 2 (2007)

Chemistry in Combustion 2 (2008)

Chemistry in Combustion 2 (2009)

Chemistry in Combustion 2 (2010)

The courses chemistry in combustion have been traditionally a backbone in the education of Biofuel GS students. These yearly recurring courses are open for GS biofuels student as well as other students at ÅA as well as students from GSCE.

The goal is to introduce industrial scale combustion systems and gas phase chemistry within them. In addition, fundamental theoretical and practical tools, including expert research software, for studying gas phase and ash chemistry.

The students learned following concept after finishing the course:

- Basic concepts of combustion
- Basic definitions and terms in combustion and combustion chemistry
- Basic knowledge about the formations of gaseous and particulate emissions
 - Basic understanding of ash related problems

Topics covered included combustion technologies, fuel properties and thermal conversion, and gaseous emissions. In addition lectures and exercises using the "Chemical Engineering Toolbox", an approach where a

combustion system is studied on four levels of increasing complexity: stoichiometry, chemical equilibrium, kinetics, and mixing.

In the second part of the course an overall introductory picture of the tools used in ash chemistry in combustion is given.

The course included subjects like studying formation of ash, deposits and corrosion, heavy metals and sootblowing. During exercises different calculation tools, such as thermodynamic and CFD modelling were demonstrated. An excursion to a black liquor boiler where we participated in a measurement campaign was arranged and acted as case study.

Thermo Chemical Conversion of Biomass and Wastes Chalmers, Göteborg 19-23 November 2007

Henrik Thunman and Bo Leckner

This course is about thermal conversion (pyrolysis, gasification and combustion) of solid biomass or wastes.

The aim is to give the participants the fundamental knowledge of how thermal converters of solid biomass and wastes are designed, why they are designed as they are and how the individual fuel particles are converted within these devices. This is presented in the form of lectures, tutorials and five assignments:

- Modelling of the covering conversion of thermal small particles
- Modelling of the conversion of thermally large particles including comparison with measurement data
- Design of a stationary (bubbling) fluidised bed
- Heat balance of a gasifier
- Heat balance of Chalmers 12 MW circulating fluidised bed boiler

The topics included are:

- Fuel characteristics
- Conversion of solid fuel
- Conversion devices
- Boilers, gasifiers and furnaces
- Energy system related to thermo chemical conversion of solid biomass and wastes

<u>Teaching</u>		<u>form:</u>
Lectures	16	h
Tutorials	16	h
Excursion	2	h
Assignments	40	h

Teachers:

Lectures: Prof. Bo Leckner, Ass Prof. Henrik Thunman
 Tutorials and assignment: M.Sc. Robert Johansson, M.Sc. Sven Hermansson

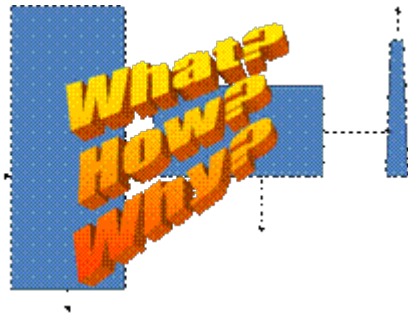
Analytical Techniques in Combustion (2008-2009)

Within the nordic countries large knowledge is available with respect to energy conversion and methods to study conversion of new challenging fuels. This knowledge is spread is not easily accessible to young researchers, i.e. PhD students.

Large scale, lab scale and analytical methods are available, but not used optimally since insufficient knowledge is available on where the equipment is located and on the advantages and drawbacks these tools can have.

By educating our PhD students within program with a “hands-on course”, these tools can become available for a large research community, networks will be formed and researchers will be trained on the highest level available.

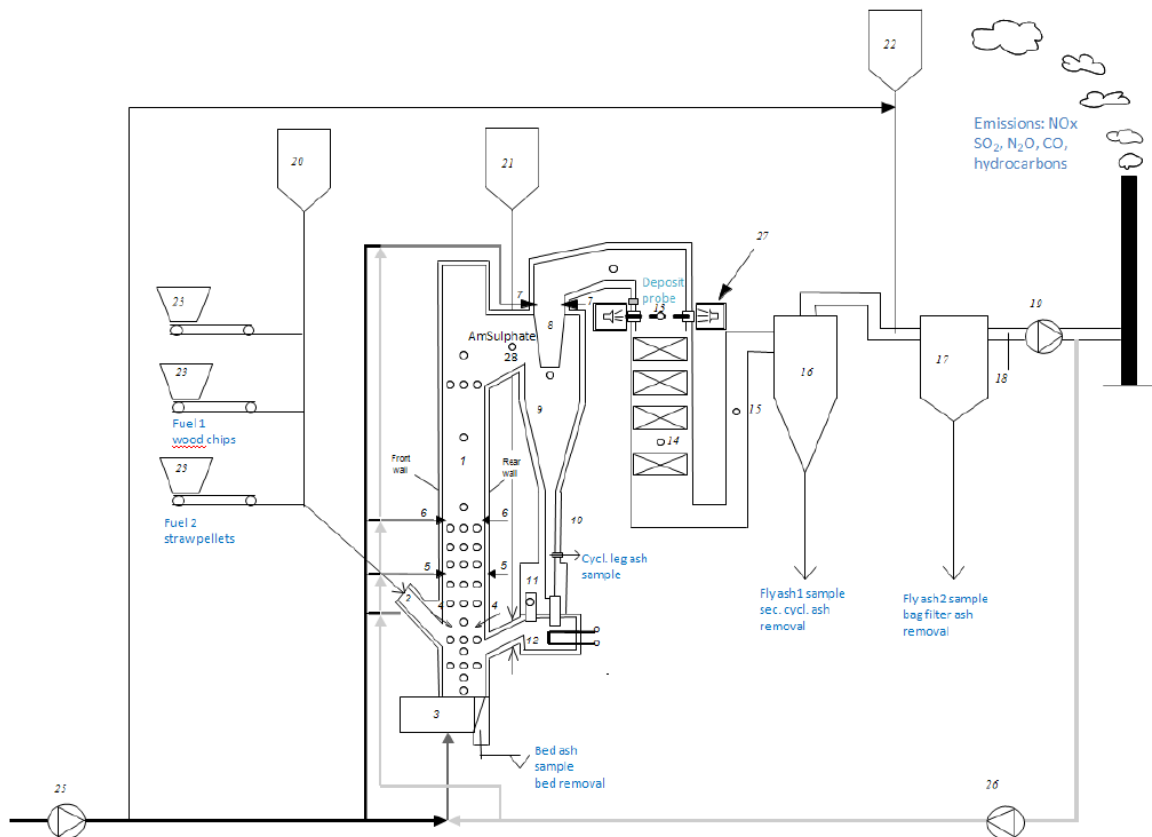
Often PhD students miss an overview of phenomena taking place in large scale facilities. By combining specialism of different partners this overview can be obtained (see figure)



At the end of the course participants should be able to critically assess research tools available in Europe and to be able to use them when valid.

16 students participated in the whole sequence of courses to be able to gain a complete overview (10ETCS).

The course consisted of several parts taking place as intensive courses at the different partners, i.e. AAU, DTU, NTNU, and CTH. Fuels were in semi-large scale facility at CTH. Fuels and ashes were collected and taken along through the course for further investigation. When possible, analyses were compared with lab scale experiments.



Effect of ammonium sulphate addition on the combustion of high chlorine and potassium biomass in a 12 MWth CFB – ash and species balance

Linda Nørskov, Samira Telschow, Hao Wu

In this study, co-firing of different biomass fuels and the effects of ammonium sulphate addition were investigated in a 12 MWth circulating fluidized bed (CFB) boiler at Chalmers University of Technology. During a two day-testing period, wood chips and straw pellets were co-combusted on the first day, and the effects of ammonium sulfate injection were evaluated under similar fuel condition on the second day. The work presented here focuses on the ash and elemental mass balances in the experiments as well as the distribution and molar ratio of different elements in different ash samples. Effects of ammonium sulfate addition on the reactions of potassium and chlorine in the biomass fuels will be discussed based on the results.

Only the mass balance for sulfur closed acceptable to about 100%. The general unsatisfactory mass balances of other elements such as K, Cl and Na indicate that the assumption of the accumulated ash composition equaling to that of secondary cyclone ash does not seem adequate.

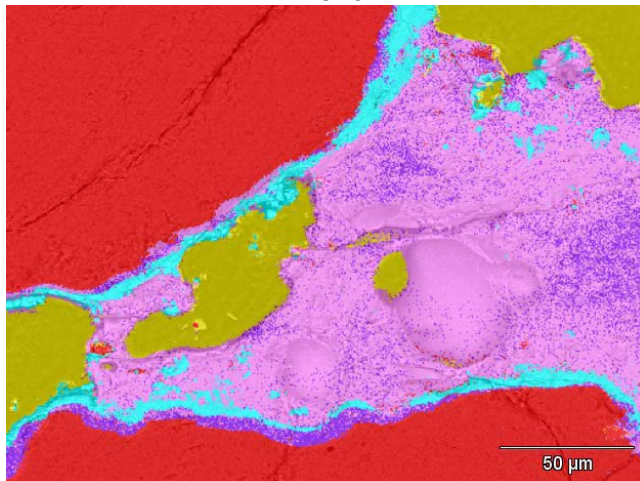
However, the mass balances clearly show that the addition of ammonium sulphate has converted part of alkali chlorides to alkali sulphates.

The distribution of the different elements in the secondary cyclone ash, bag filter ash, accumulated ash, and emissions is estimated. It is found that the majority of alkali and chlorides are accumulated in the boiler when no additive is used. The ammonium sulphate additive significantly reduces this accumulation, however approximately 30% of the chlorine which is found in secondary cyclone ash and bag filter ash does not undergo the gaseous sulphation reaction despite a large excess of sulfur present. The nearly no accumulation of chlorine in the boiler is most likely a result of both solid phase and gaseous sulphation reaction.

Molar ratios of the elements of interest are made for the fuel mixture and ash samples. The increase of sulphate containing molar ratios when adding ammonium sulphate in the second day experiments indicate that the corrosion and deposits caused by alkali chlorine is negligible.

Bed agglomeration in a 12 MWth CFB boiler when co-firing wood chips and straw pellets

Frida Claesson, Patrycja Piotrowska, Oskar Karlström, Johan Lindholm



In this work, bed agglomeration was investigated when co-firing different biomass fuels in a 12 MWth CFB boiler at Chalmers University of Technology. The boiler was run for two days. During the first day wood chips and straw pellets were co-fired.

During the second day the same fuels were co-fired with an addition of ammonium sulfate (later referred to as day 1 and day 2).

Bed material and cyclone leg samples were collected and analyzed by means of Scanning Electron Microscope with an Energy Dispersive X-ray analyzer (SEM/EDX). The SEM/EDX results were compared with chemical fractionation results of the co-fired fuels. The SEM examinations of the samples showed that a coating with a thickness of around 30 μm was formed around the bed material particles and the circulating bed particles.

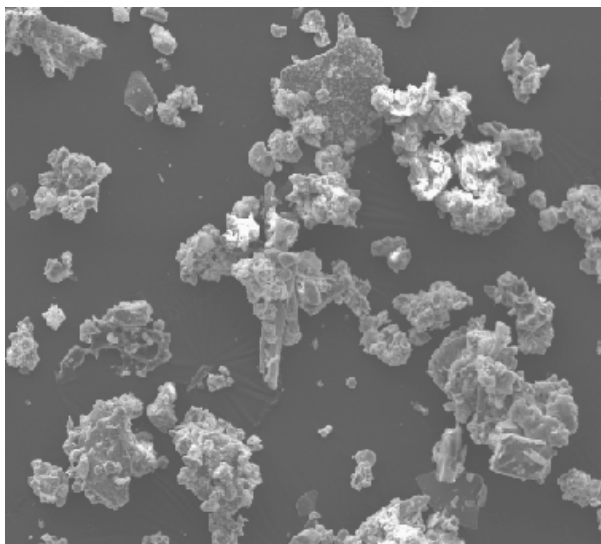
The coating consisted of several layers. The layers closest to the silica core were rich in potassium and silica, indicating a formation of potassium silicates. On the top of the potassium-rich layer a calcium-rich layer was found. The outermost layer showed a composition consisting of elements similar to those in the fuel ash. The SEM results were compared with fuel fractionation results. The elements found in the water and acetate fractions seem to be found in the outermost layer of the coated sand particles. In the coatings, no significant differences were found between the bed material particles and the circulating bed particles. Furthermore, no influence of ammonium sulfate addition on bed agglomeration was observed.

Agglomerates could be found in the bed samples indicating that bed material agglomeration took place in the boiler during the tests. SEM/EDX analysis of their crosssections showed that potassium silicates acted as the adhesive agent.

SEM/EDX Analysis of Deposit Rings and Cyclone Fly Ash

Muhammad Shafique Bashir, Norazana Ibrahim, Kavitha Pathmanathan

In the present study, potassium, chlorine and sulphur chemistry, and the transport and the distribution of these species in Circulating Fluidized Bed (CFB) boiler is analyzed.



The impact of ammonium sulphate as additive on fly ash composition and corresponding effect on ash deposition rate has been evaluated. The fly ash samples and the deposits obtained on deposit ring were analyzed by Scanning Electron Microscopy (SEM) equipped with Energy Dispersive X-ray (EDX) technique. The addition of ammonium sulphate as an additive in the combustion zone of a boiler has shown a positive effect. The

addition of the additive has successfully reduced the amount of deposits formed by reducing the formation of KCl. The SEM/EDX analysis of the deposits formed shows that the addition of the additive plays a vital role in converting the alkali chlorides to alkali sulphates. The most favorable

reduction is of Cl. There formation of Cl in the deposit has been totally eliminated via the formation of K_2SO_4 . This reaction has also favored in the reduction of the KCl formation.

The SEM/EDX analysis of the fly ash samples from the secondary cyclones shows that the amount of S has increased almost by 50% with the addition of additives. This can be contributed by the S element present in the ammonium sulphate. A major conclusion can be drawn by stating that the addition of the ammonium sulphate has reduced the formation of deposits which is one of the most important factors in the boiler.

Co-Combustion of Wood and Straw in a Circulating Fluidized Bed Boiler

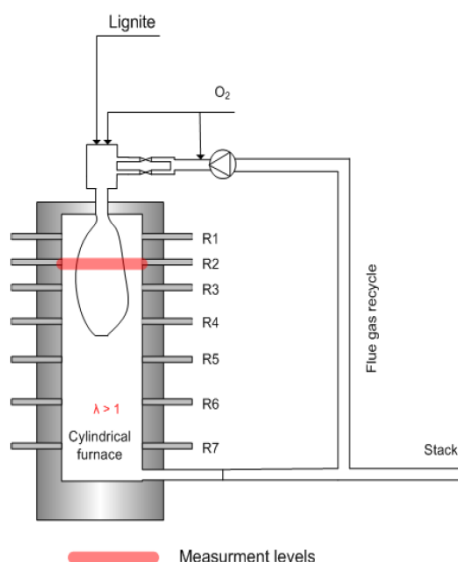
– reduction of NO_x emission

Johanna Olsson, Fredrik Lind, Pontus Markström

The nitrogen oxides (NO_x) reduction through selective non-catalytic reduction in the flue gas stream from the co-combustion of wood chips and straw pellets in a circulating fluidized bed boiler has been investigated. Injection of ammonium sulphate (AmSulphate) to the inlet of the hot cyclone decreases the emissions of NO_x but a low overall efficiency for the reduction process is obtained in this work. No ammonia-slip (increased concentration of ammonia in the flue gas) was observed when the ammonium sulphate was added

FTIR measurement of NH_3 , HCN, SO_2 , H_2S and COS in pulverized lignite oxy-fuel flames

Daniel Fleig, Stefan Hjærtstam and Daniel Kühnemuth



Nitrogen and sulphur compounds are investigated in the atmosphere of a high temperature oxy-fuel flame, using Fourier Transform Infrared Spectroscopy (FTIR). For this application, evaluation routines have been developed to investigate the concentrations of NH_3 , HCN, SO_2 , H_2S and COS by analyzing the absorption intensity of characteristic fingerprints

within the strong overlapping of the CO₂ rich sample gas matrix.

NH₃ and SO₂ was successfully analysed however HCN, H₂S and where not measured. The later species had either low concentration at the specific spatial measurement point or could not be detected due to too strong overlapping from absorption bands other gases in the same wavelength.

It is furthermore discussed if decomposition of HCN, H₂S and COS on the filter of the sampling probe or elsewhere during the sampling process could cause the noticed difficulties in detectability of those gases.

Students – 2010

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TOPIC	Characterization and Quantification of Deposits Buildup and Removal in Straw Suspension-Fired Boilers
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MAIN SUBJECT	Biomass combustion and deposit related problems
SUPERVISORS	Professor Kim Dam-Johansen Associate Professor Peter Arendt Jensen Associate Professor Flemming Frandsen Associate Professor Stig Wedel
M.Sc.	April 2008
DOCTORAL STUDIES	
Started	September 2008
To be completed	August 2011

Characterization and Quantification of Deposits Buildup and Removal in Straw Suspension-Fired Boilers

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Background

Compared to coal ashes, the biomass-derived ashes contain significant amounts of potassium and chlorine, and the use of biomass, primarily straw, in power plant boilers is a serious technical challenge [1, 2]. The potassium components during straw combustion play a significant role in the deposit formation because they act as glue bonding the individual fly ash particles together [2]. The deposit formation is a dynamic process, and consists of both deposit growth [3, 4] and removal processes [3, 4, 5]. The mechanisms by which ash deposits formed are: condensation, diffusion, thermophoresis, inertial impaction and chemical reaction. The major contributing process for deposit build up is inertial impaction when large particles ($> 5 \mu\text{m}$) have too large inertial momentum to follow the gas streamlines around the tube and instead impact on the surface. The capture efficiency of the particles depends on the size and density of the particle, the viscosity of the outer layer of the particle plus the deposit surface layer morphology and viscosity. When pure straw fuel is utilized in large suspension-fired boilers the heat transfer surfaces may be covered by severe ash deposits, impeding the plant operation. The deposit formation and removal (shedding) in biomass-fired boilers has been the objectives of some previous studies [4]; however some biomass deposit related processes are still not well described. Most studies have been based on measurements in grate boilers, while only limited data are available from biomass suspension-firing where improved knowledge on the transient deposit formation process, the influence of fuel characteristics and mechanisms of ash deposits removal are needed. From a scientific point of view, the quantification of ash deposit build up and removal naturally and/or by sootblowing in suspension-fired boilers is an area where relatively limited accurate knowledge is available [4, 6].

Objectives

The objective of this project is to provide recommendations for the optimal operation strategy of suspension-fired straw boilers with respect to minimization of deposit related problems. The specific objectives of the project are:

- Understanding removal behavior of deposits in the boiler chamber and superheater region (convective pass) of biomass- fired boilers.
- Investigating the influence of load, operation conditions and fuel changes (straw, wood or coal firing) on boiler deposits.
- A model based description of the influence of fuel changes on deposits. The model needs to account for deposit formation and

removal with changed temperature, ash composition and flow conditions.

- Provide measuring data that can support activities on fuel characterization and CFD modeling.

Methods

Full scale experiments were conducted in 2009 at Amagerværket Biomass Suspension-fired Boiler Unit 2 (AMV2, 250 MW_{th}) and in 2010 at newly commissioned Amagerværket Biomass Suspension-fired Boiler Unit 1 (AMV1, 350 MW_{th}). A double annular probe made of stainless steel, with a total length of 3 m and an outer diameter of 40.5 mm was used during the experiments. A load cell was used to detect variations of the force caused by the mass of the ash deposit on the probe inside the boiler. A charged-couple device (CCD) camera registered the deposit formation and removal process on the probe. The flue gas temperature near the probe was continuously measured, using a simple thermocouple in a protective shell. A suction pyrometer (IFRF [7]) was used during different intervals in almost each experiment in order to confirm the accuracy of the flue gas temperature measurements. An artificial sootblowing probe with an external diameter of 42.2 mm and 3 m length was used for in-situ removal of deposits. The sootblower nozzle was fixed at the end of the probe. Peak Impact Pressure (PIP) through the nozzle was measured along the axial centerline as a function of the supplying air pressure using pitot tube.

A series of short (0.5-4 h) and long (3-18 days) duration deposit probe experiments were conducted utilizing 0% to 100 % straw with wood on mass basis at different boiler loads.

Results

Deposit Buildup

Important findings related to deposit build up were:

- The fouling and slagging propensity during co-combustion of straw and wood was reduced to that for pure straw possibly due to dilution effect and change in the elemental composition. When straw share was greater than 40 % on mass basis in the fuel, the flue gas temperature was the key factor controlling the deposition rate.
- With increase in probe surface temperature from 500 °C to 600 °C, the deposit mass uptake increased possibly due to partial melting of the condensed salt layer.
- Deposits were more sintered in the windward direction during pure straw-firing.
- It was also observed that the final deposit weight uptake was not higher compared to biomass grate-firing at almost similar conditions.

Deposit Shedding

Image analysis of all experiments reveals that deposit shedding was primarily through debonding in the superheater region of suspension-fired

boilers. It was also found that increase in exposure time and probe metal temperature increased the PIP needed to remove the deposits. As shown in Figure 1 deposits of less than 91 h exposure time were easy to remove and PIP needed was less than 55 kPa at 500 °C probe metal temperature. With increase in probe surface temperature from 500 °C to 600 °C, PIP needed to remove the deposits increased. Higher probe surface temperature caused melting of inner most layer and the adhesion strength between the deposit and the tube was enhanced. At higher probe surface temperatures (> 550 °C), 2-10 mm thick layer was formed in the rear surface and was being attached to the thick front layer, making difficult removal of the windward layer. At lower temperatures (< 500 °C), the layer formed in the rear side was thin and the distinct front layer was easy to remove using artificial sootblower.

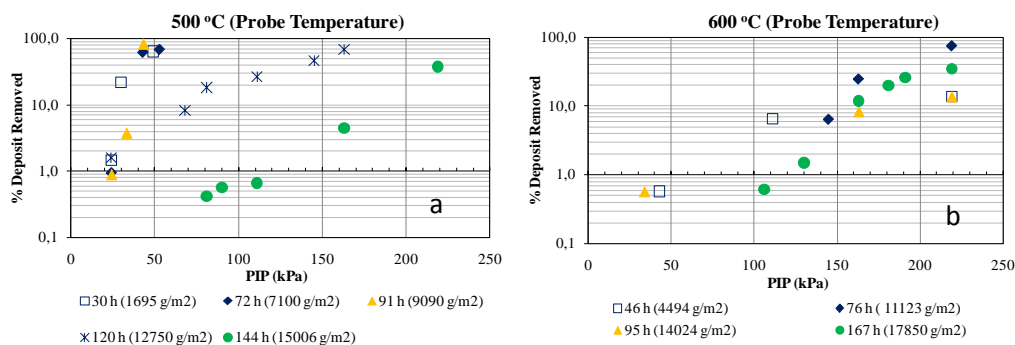


Figure 1: Influence of probe exposure time and probe metal temperature on deposit removal for different weight uptake signals a) 500 °C probe metal temperature; b) 600 °C probe metal temperature.

Residual Ash and Deposits Characterization

Elemental analysis of residual ashes and deposit samples was made in order to determine concentrations of the major elements such as Al, Ca, Fe, K, Mg, Na, P, Si, S and Cl using both SEM/EDX and ICP-OES. It was identified that the straw suspension-firing fly ashes contain high contents of Si and Ca, while grate-firing fly ashes contain higher contents of volatile elements such as K, Cl and S. Chemical analysis of the probe front side deposit samples during 35% straw-firing and 100% straw-firing indicated that the contents of S, K and Cl increased while Ca and Mg contents were reduced by increasing the straw share. K and S contents were found at higher percentages in the innermost layer of the probe, possibly attached in the form of condensed salts and through thermophoresis.

The detailed elemental analysis of fuel ash, fly ash, and bottom ash and deposit samples is being carried out now-a-days at Vattenfall Laboratory and at CEN DTU (Detailed elemental analysis of fuel ash, deposits, and residual ash will be presented for short and long run experiments at different boiler loads and straw shares at 500, 550 and 600 °C probe metal temperature). Full scale measurements using the horizontal and newly designed vertical probe will be made in the coming year with the objective to quantify and characterize deposit build up and removal in the

superheater region and furnace region of a straw and wood suspension-fired boiler.

Based on the current findings, recommendations for the optimal operation strategy of straw and wood suspension-fired boilers with respect to minimization of deposit related problems can be provided.

Publications and Presentations:

[1] M. S. Bashir, P. A. Jensen, F. Frandsen, S. Wedel, T. Wolfe, K. Dam-Johansen, S. T. Pedersen and J. Wadenbäck, OA5.1, (2010), 18th European Biomass Conference, 03-07 May, Lyon, France.

[2] M. S. Bashir, P. A. Jensen, F. Frandsen, S. Wedel, K. Dam-Johansen, S. T. Pedersen and J. Wadenbäck, 2010, Impact of Fuel Quality on Power Production and the Environment, 29-03 Sep. Ivalo, Finland.

[3] M. S. Bashir, P. A. Jensen, F. Frandsen, S. Wedel, K. Dam-Johansen, T. Wolfe, S. T. Pedersen and J. Wadenbäck, 2010, Dansk Kemiingeniør Konference - DK2 , 16-17 June, Lyngby, Denmark.

Participation in GS biofuel courses and seminars

Adjungerad (fr.o.m. juni 2009, 2010)

[1] Analytical Techniques in Combustion, PhD course, 10 ECTS.

Participation in the four parts of the entire course was made according to the following schedule;

Part I: Chalmers, Gothenburg, Sweden, October 22-26, 2008. Main focus on full-scale tests at biofuels (wood and straw) based Chalmers' Circulating Fluidized Bed Combustion (CFBC) boiler.

Part II: DTU, Lyngby, Denmark, February 2-6, 2009. Focusing on entrained flow and swirl flow combustion experiments and SEM/EDX analysis of deposit samples collected from measurements at Chalmers boiler.

Part III: NTNU, Trondheim, Norway, May 4-8, 2009. Main focus on fuel characterization by Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA).

Part IV: Åbo Akademi, Finland, September 21-25, 2009. Fuel characterization by chemical fractionation analysis. Experiments using straw and wood pellets at single particle combustion reactor.

[2] Biofuels Graduate School Annual Meeting, June, 2009, Trondheim, Norway.

Travelling

[1] Chalmers, Gothenburg, Sweden, October 22-26, 2008, Graduate School Course participation.

[2] NTNU, Trondheim, Norway, May 4-8, 2009, Graduate School Course participation.

[3] Åbo Akademi, Finland, September 21-25, 2009, Graduate School Course participation.

[4] Biofuels Graduate Annual Meeting, June, 2009, Trondheim Norway.

[5] Conference Participation, Impact of fuel quality on power production and the environment, 29-03 September, 2010, Ivalo, Finland.

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- [1] M. S. Bashir, P. A. Jensen, F. Frandsen, S. Wedel, K. Dam-Johansen, T. Wolfe, S. T. Pedersen and J. Wadenbäck, OA5.1, (2010), 18th European Biomass Conference, 03-07 May, Lyon, France.
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TOPIC **Flash Pyrolysis of Agricultural Residues**

MAIN SUBJECT **Bio oil from Flash Pyrolysis of
Agricultural Residues**

SUPERVISORS Professor Kim Dam-Johansen
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M.Sc. July 2006

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Started July 2007

To be completed Dec 2010

Flash Pyrolysis of Agricultural Residues

Norazana Ibrahim

Background

For the last decades, flash pyrolysis process has become a subject of intense research with an objective to maximize the organics liquid yields. The process is a promising thermal conversion route of biomass to produce a nearly ash-free liquid fuel with a high volumetric energy density. During pyrolysis, biomass is thermally decomposed without an oxidizing agent to produce solid charcoal, liquid oil and gases. The char contains most of the inorganic components and it can be used as an energy carrier or as a soil fertilizer. Whereas, the pyrolysis gas, which consists mainly of carbon monoxide, carbon dioxide and light hydrocarbons, can be used to generate electricity or to provide heat for the pyrolysis process. The liquid oil, on the other hand, which is also known as a pyrolysis liquid, bio-oil or tar and has a lower heating value of 15-20 MJ/kg, about half that of conventional fuel oil can be directly used without any upgrading as a fuel oil in many combustion applications such as boilers.

The yields of end products of pyrolysis are dependent on several operating parameters including temperature, types of biomass, particle size, reaction condition, and reactor configuration, as well as the extraneous addition of catalysts. The works [1-3] demonstrated that high heating rates of the biomass particles and a short gas residence time at temperature of 450 – 600 °C are required to obtain the highest possible liquid yield. Depending on the feedstock and operating conditions, the flash pyrolysis of wood produces 50-75 wt % of liquid bio-oil (including water), 15-25 wt % of solid char and 10-20 wt % of non-condensable gases [4,5].

The bio-oil product of a flash pyrolysis process is not thermodynamically stable under different storage temperature due to the flash pyrolysis itself is not an equilibrium process. During storage, the chemical composition of the bio-oil which is a mixture of oxygenated hydrocarbons with a wide range of molecular weights will change toward thermodynamic equilibrium, resulting in changes in viscosity, molecular weight, water content and co-solubility of the most compounds. Furthermore, the simple phase of bio-oil can separate into various tarry, sludgy, waxy and a thin aqueous phase during aging. Researchers [6-8] have demonstrated that the oil viscosity and instability may be reduced through the use of several techniques such as hydrodeoxygenation, emulsifications and as well as the use of catalyst to the pyrolysis oil. Several factors also need to be taking into consideration during the combustion applications such as water content, oxygen content, wide volatility distribution, char content in the pyrolysis oil, which negatively impact the atomization, ignition, coking tendency, and emissions associated with burning this bio-oil.

Objectives

The main objective of this research is to optimize the bio-oil production of flash pyrolysis process from different agricultural residues (wheat straw and rice husk) and pine wood. The optimization is performed by considering the effect of the pyrolysis temperature, feedstock initial moisture content and types of biomass used. In addition, the storage and stability of bio-oils product is investigated by monitoring the changes of its physical and chemical properties over the storage conditions. Finally the combustion properties of the bio-oils are also studied.

Method

1. Flash pyrolysis experiment

Pyrolysis of wheat straw, pine wood and rice husk were carried out in a bench scale of Pyrolysis Centrifuge Reactor (PCR) [9] developed at CHEC DTU, by using flash pyrolysis reactor as shown in Figure 1. The principle of the process is by tangentially feeding solid biomass particles into the horizontally oriented $\text{Ø } 82 \times 200$ mm tubular reactor.

The centrifugal force created by the rotation of three blade rotors keeps the particles sliding on the heated wall while passing through the reactor. The solid particles transform to vapors by the high efficiency of heat transfer and while undergoing reaction, particles move down the reactor pipe before leaving suspended in the gas through the tangential outlet. Larger char particles were removed by a change-in-flow separator whereas fines were collected by the cyclone.

Vapors were condensed in a direct water cooled condenser (bubble chamber) filled with previously produced bio-oil. Aerosols that were not retained by the condenser were collected in a coalescer filled with ROCKWOOL (fibers). The gas was pumped to the preheater and heated to 400 °C before it is recirculated to the reactor in order to maintain a desired gas residence time and avoid condensation of liquid products within the reactor. The amount of produced gas was measured by a temperature compensated gas meter and a sample was collected in a gas bag.

In this work, the biomass feedstock was fed to the reactor of approximately 20-23 g/min and with an approximately gas residence time of 0.3 s, a particle residence time of 180 s and an initial heating rate of approximately 250-1000 °K/s. The performed measurements made it possible to determine the yield of char, gas, water and oil of the single measurements.

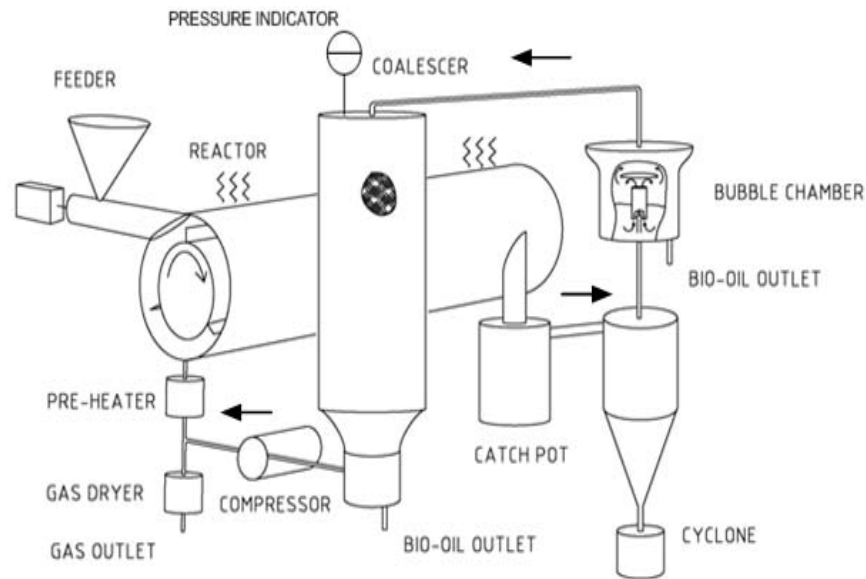


Figure 1: Schematic diagram of pyrolysis centrifuge reactor (PCR).

2. Bio-oil storage stability

In this study, bio-oil pyrolyzed from wheat straw and pine wood were used. Both feedstocks were pyrolyzed at their optimum conditions (i.e. straw pyrolyzed at 525 °C and pine wood pyrolyzed at 550 °C). 50 grams of each bio-oil was prepared and stored at three different temperatures, at room temperature, at 50 °C and at 80 °C, in a closed glass vessel and at air exposed conditions (in an open glass vessel). For the open glass vessel method, air was bubbled through the samples approximately 3 minutes, once a day for 5 days/week.

The changes in water content (Karl Fisher titration method), heating value (bomb calorimeter), pH (standard pH meter), molecular weight (Gel Permeation Chromatography) and viscosity (Automated Microviscometer AMV 200 instrument) of bio-oils were determined as a function of storing temperatures, open/closed glass vessel and length of storage.

Results

1. Flash pyrolysis experiment

i. Moisture Content

- The experimental results show that the changes in straw moisture content have no significant effect on the distribution of pyrolysis product yields. The effect of straw moisture on char yield only can be observed at lower temperature. The optimal reaction temperature for the production of bio-oil was around 525 °C to 550 °C for all straw moisture contents.
- The water content in bio-oil increased with increasing of straw moisture content.

- The energy distributions of bio-oil, char and gas were around 56-69 %, 24-33 %, and 2-19 %, respectively.

ii. *Pyrolysis Temperature*

- Apparently, the pyrolysis temperatures have a dominant effect on the pyrolysis product yields. In general, the yield of liquid organics increased with increasing pyrolysis temperature from 475 °C to 550 °C and then decreased at higher temperatures.
- The gas yield kept increasing with reactor temperature due to secondary cracking takes place at higher temperatures, which in turn lead to a reduction of the liquid organics yield and an increased production of light hydrocarbon gases.
- There were no affect on produced water yield with increasing temperatures.

iii. *Types of Biomass (wheat straw, rice husk and pine wood)*

- The maximum organics yield for straw occurred at 525 °C and at 550 °C for both rice husk and pine wood.
- The presence of alkali matters in biomass ash especially potassium and sodium reduce the yield of liquid organics by catalytic decomposition of tar and also lowering the optimum yield temperature.

2. *Bio-oil Storability*

- From this study, it is found that storing the bio-oils at room temperature with a proper sealed glass vessel remains its original properties for at least 130 days. The results also showed that the rate of aging was higher and occur faster when stored the bio-oil at higher temperatures.
- pH and heating value of all bio-oil samples were not change significantly during the aging test.

Publications and Presentations:

[1] N.Ibrahim, P. A. Jensen and K. Dam-Johansen. Effect of biomass mineral matter on the pyrolysis product yields. Proceeding of the 18th European Biomass Conference and Exhibition, Lyon France 3 -7 May 2010, PP 1022-1026.

[2] N.Ibrahim, N.Bech, P. A. Jensen and K. Dam-Johansen. Influence of water content on wheat straw pyrolysis. Submitted for publication, 2010.

[3] Esben W. Bruun, Henrik Hauggaard-Nielsen, Norazana Ibrahim, Helge Egsgaard, Per Ambus, Peter A. Jensen, Kim Dam-Johansen. Influence of fast pyrolysis temperature on biochar labile fraction and carbon sequestration. Submitted for publication, 2010.

Participation in GS biofuel courses

[1] Conversion of Solid Biomass and Waste, PhD course, 5 ECTS.

[2] Analytical Techniques in Combustion, PhD course, 10 ECTS.

Participation in the four parts of the entire course was made according to the following schedule;

Part I: Chalmers, Gothenburg, Sweden, October 22-26, 2008. Main focus on full-scale tests at biofuels (wood and straw) based Chalmers' Circulating Fluidized Bed Combustion (CFBC) boiler.

Part II: DTU, Lyngby, Denmark, February 2-6, 2009. Focusing on entrained flow and swirl flow combustion experiments and SEM/EDX analysis of deposit samples collected from measurements at Chalmers boiler.

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Part IV: Åbo Akademi, Finland, September 21-25, 2009. Fuel characterization by chemical fractionation analysis. Experiments using straw and wood pellets at single particle combustion reactor.

Travelling

[1] Chalmers, Gothenburg, Sweden, November 19-23, 2007, Graduate School Course participation.

[2] Chalmers, Gothenburg, Sweden, October 22-26, 2008, Graduate School Course participation.

[3] NTNU, Trondheim, Norway, May 4-8, 2009, Graduate School Course participation.

[4] Åbo Akademi, Finland, September 21-25, 2009, Graduate School Course participation.

[5] Conference Participation, 18th European Biomass Conference and Exhibition, 3-7 May 2010, Lyon, France.

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[1] N. Ibrahim, P. A. Jensen and K. Dam-Johansen, (2010), 18th European Biomass Conference, 03-07 May, Lyon, France.

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TOPIC **Fuel flexible rotary kilns for cement
production**

MAIN SUBJECT **Combustion Chemistry**
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Fuel flexible rotary kilns for cement production

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Background

Cement production is highly energy intensive. The global energy consumption by the cement industry is about 10 times the total energy consumption of Denmark [1, 2]. Coal and coke have traditionally been the primary fuels in the industry, but increasing fossil fuel prices and environmental concerns make other fuels attractive. Since energy costs accounts for 30-40% of the total costs of cement production, there is a great potential to reduce the overall production costs by replacing fossil fuels with alternative fuels. In this context "alternative fuels" refers to all non-fossil fuels and waste from other industries. Secondary, waste or replacement fuels are often used as synonyms for alternative fuels. Alternative fuels are typically cheaper than fossil fuels and in some cases the cement producer may even be paid to receive the alternative fuels.

Substitution of fossil fuels with alternative fuels offers the following major advantages:

1. Alternative fuels may be CO₂ neutral.
2. Fuel costs are typically reduced.
3. Solid residues from the alternative fuels are incorporated into the cement.
4. High flame temperatures and residence times provide good conditions for destruction of organic compounds.

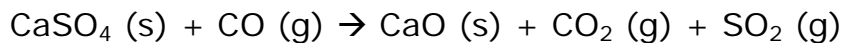
In the recent years the use of alternative fuels has increased. In Germany, for example, the share of alternative fuels is today higher than 56%, while it was only 4% in 1987 [3, 4]. It is expected that the share of alternative fuels will continue to increase in the coming years, which will create a need for new technology to handle, treat and combust these fuel types.

Many types of alternative fuels are applied in the cement industry. The majority of the alternative fuels are on solid form, while liquids and gasses are less common. Some of the most common alternative fuels are refuse derived fuels (RDF, a mixture of house hold waste and industrial waste), tyre derived fuels (TDF), meat and bone meal (MBM) and waste wood. Technical feasibility, public acceptance, price and availability are typically the determining parameters for the type of alternative fuel that will be utilised at a specific cement plant.

It is attractive to fire coarse, solid alternative fuels into the material inlet end of cement rotary kilns in order to save expenses for shredding of the fuels to smaller particles and to increase flexibility. High temperatures in the rotary kiln and material retention times of 15-25 minutes provide good conditions for fuel burnout.

The main challenge is, however, that the solid fuel particles will be in physical contact with the cement raw materials: If the fuel particles are fully or partly covered by cement raw materials, mass transfer of oxygen to the fuel char will be hindered. Lean amounts of oxygen will lead to incomplete oxidation of the fuel char, forming reducing agents such as CO.

Local reducing conditions in the raw material charge are known to affect the product quality and process stability of the kiln system. The product quality can be influenced by raw material components such as Fe(III) being reduced to Fe(II). Fe(II) affects the formation of belite ($2\text{CaO}\cdot\text{SiO}_2$) and alite ($3\text{CaO}\cdot\text{SiO}_2$), the two strength-giving components in cement. The process stability is affected by increased release of sulphur from the raw materials, mainly by decomposition of CaSO_4 :



SO_2 may react with alkali salts, forming eutectic salt mixtures which stick to the walls. Dust can adhere to this sticky layer and lead to deposit build-ups. These deposit build-ups accumulates typically in the material inlet end of the rotary kiln, or in the riser duct between the calciner and rotary kiln, where they lead to blockages that requires temporarily plant shut-down to remove.

Objectives

The overall success criterion is to develop scientific based knowledge for precise prediction of the use of different alternative fuels in the rotary kiln inlet.

More specific success criteria:

- 1: Identify optimal rotary kiln design(s) for combustion of coarse, solid alternative fuels and at the same time maintain optimal conditions for clinker burning.
- 2: Identify limitations for solid alternative fuel quantities to be fired in rotary kilns in order to ensure optimal clinker burning.
- 3: Investigate and describe how combustion of solid alternative fuels in the back-end of rotary kilns will affect the process stability of the kiln system. It will particularly be studied how local reducing conditions in the rotary kiln may lead to increased deposit build-ups in the kiln system.
- 4: Investigate and describe what types of alternative fuels that are most suitable for combustion in the back-end of rotary kilns.
- 5: Suggest ideas and concepts for patenting new technology that can optimize the flexibility regarding combustion of alternative fuels in rotary kilns or additional combustion equipment.

Method

The experimental work has been made in a room temperature steel/plexi glass rotary drum at FLSmidth A/S as well as in a fixed bed reactor at DTU. A new high temperature rotary drum, see figure 1, has been

constructed during 2009 and 2010 and is currently used to study fuel/raw material interactions during fuel combustion.

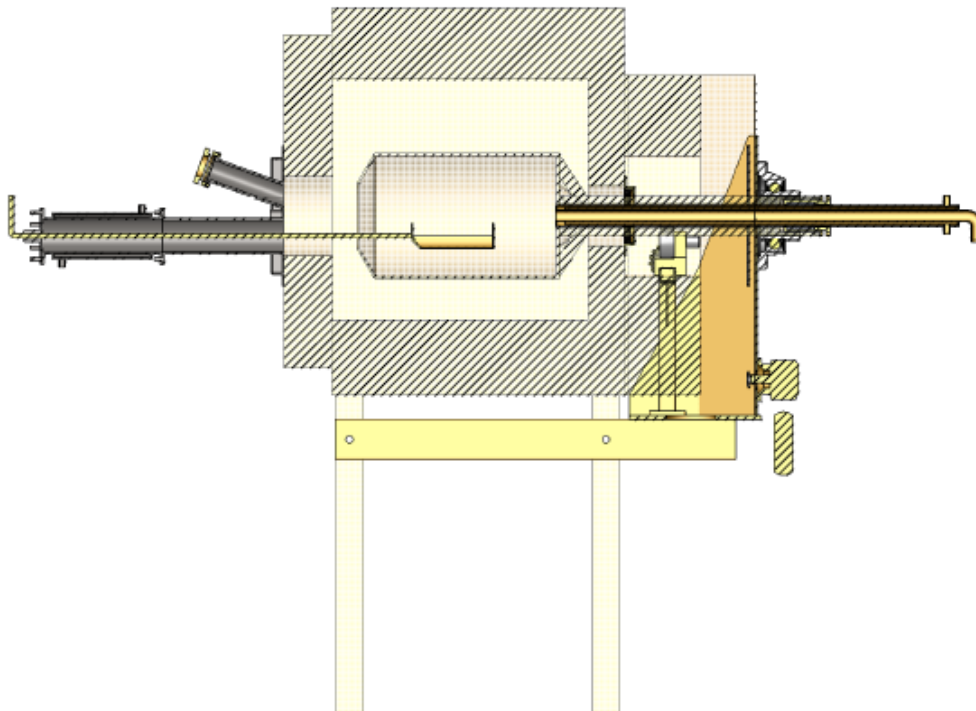


Figure 1: High temperature rotary drum for simulation of combustion processes in the material inlet end of cement rotary kilns.

Results

Mixing of solid fuel particles and cement raw materials have been studied in order to clarify the influence of fuel particle size and shape, rotary drum filling degree and rotational velocity on the way the fuel particles distribute in the material charge. The results indicate that even large fuel particles will quickly be fully or partly covered by raw materials in a rotary kiln. This has consequences for the heat up and burn out time of the fuels: Fuel particles may mainly be heated by conduction from the raw materials and the combustion will be diffusion limited due to poor oxygen mass transfer. A clear tendency was observed that large fuel particles were less covered by raw materials than smaller fuel particles.

Release of sulphur from calcined cement raw materials under both oxidizing and reducing conditions were investigated. The investigations included thermodynamic equilibrium calculations in the temperature interval 800-1,500°C and experiments in a high temperature tube furnace reactor in the temperature interval 900-1,100°C. The investigated conditions resembled actual conditions in the material inlet end of cement rotary kilns. It was found that the sulphates CaSO_4 , K_2SO_4 and Na_2SO_4 were all stable under oxidizing conditions, but began to decompose under reducing conditions. Particularly CaSO_4 was sensitive to reducing conditions. The experimental results have given inspiration to develop a method to minimize sulphur release from calcined raw materials. A patent application has been written for this method.

Combustion experiments with the fuels tyre rubber, wood, poly propylene and pet coke has been made in the high temperature rotary drum. It is observed that the devolatilization time for these fuels are only slightly affected by parameters such as the raw material fill degree and drum rotational speed, while both parameters were observed to have a great influence on the time for char oxidation. Figure 1 show the time for full conversion for a cylindrical tyre rubber particle when the raw material fill degree is 0%, 5% and 10%, respectively. The conversion time is observed to be approximately 100 seconds in the empty rotary drum and 210 seconds with 5% fill. When the fill degree is 10%, the conversion time is approximately 670 seconds. These observations indicate that the fuel conversion is greatly affected by diffusion limitations through the raw material bed.

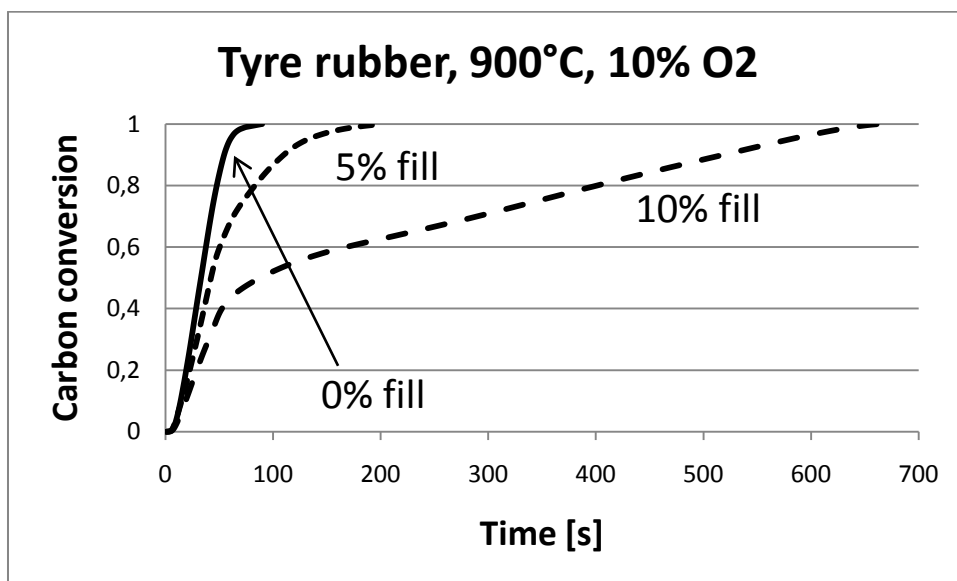


Figure 2: Effect of raw material fill degree on the conversion time for a cylindrical tyre rubber particle with dimensions (DxL) = 9x25 mm. The bed material is coarse quartz sand. Gas flow = 100 NL/min. Drum rotational speed = 6 rpm.

Figure 3 shows the effect of drum rotational speed on the conversion time for tyre rubber. It is observed that the conversion time increases with decreasing rotational speed. The conversion time is for example 375 seconds at 20 rpm while it is 810 seconds at 3 rpm. The effect of rotational speed on the conversion time may be explained by an improved gas-fuel contact at higher rotational speeds.

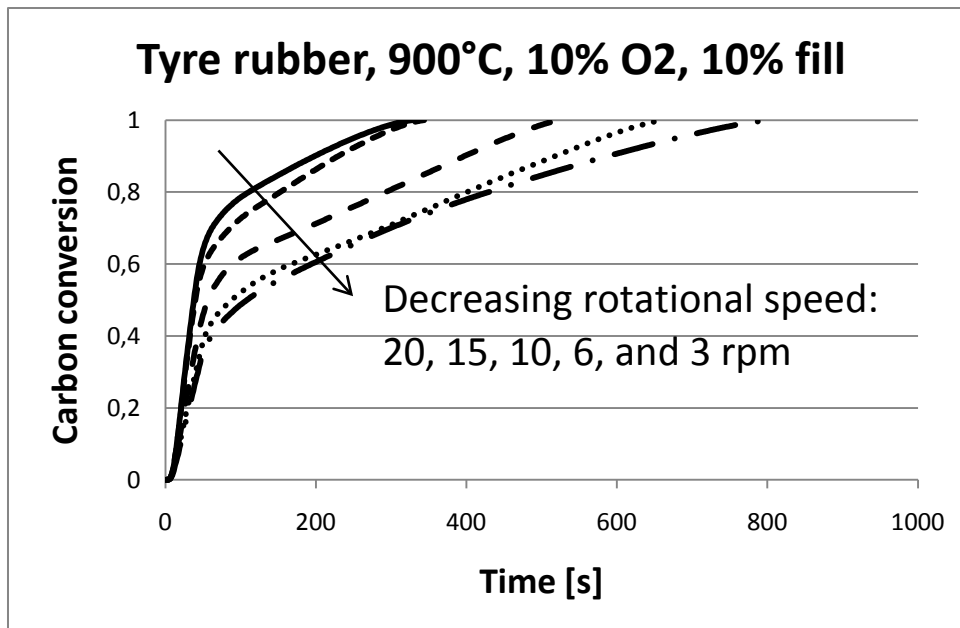


Figure 3: Effect of drum rotational speed on the conversion time for a cylindrical tyre rubber particle with dimensions (DxL) = 9x25 mm. The bed material is coarse quartz sand. Gas flow = 100 NL/min.

Publications and Presentations:

Publications:

1. Anders Rooma Nielsen, Kim Dam-Johansen, Peter Glarborg and Morten Boberg Larsen. Fuel flexible rotary kilns for cement production. Graduate Schools Yearbook 2008, DTU Chemical Engineering, Lyngby, Denmark, 101-102, 2008.
2. Anders Rooma Nielsen, Kim Dam-Johansen, Peter Glarborg and Morten Boberg Larsen. BiofuelsGS-2, Annual Report 2008-2009. Åbo Akademi University, Finland, 91-94, 2009.
3. Anders Rooma Nielsen, Kim Dam-Johansen, Peter Glarborg, Jytte Boll Illerup and Morten Boberg Larsen. På vej mod en grønnere cementproduktion. Dansk Kemi, 18-20, januar 2010.
4. Anders Rooma Nielsen, Kim Dam-Johansen, Peter Glarborg and Morten Boberg Larsen. Fuel flexible rotary kilns for cement production. Graduate Schools Yearbook 2009, DTU Chemical Engineering, Lyngby, Denmark, 117-118, 2009.
5. Anders Rooma Nielsen, Kim Dam-Johansen, Peter Glarborg and Morten Boberg Larsen. Fuel flexible rotary kilns for cement production. Dansk KemiingeniørKonference 2010. DTU Chemical Engineering, Lyngby, Denmark, 33-34, 2010.

Presentations:

1. Fuel flexible rotary kilns for the cement industry. CHEC Annual Day 2008. Søpavillionen, Hørsholm, Denmark.
2. Fuel flexible rotary kilns for the cement industry. Nordic Biofuels Annual Day 2009. Trondheim, Norway.
3. Fuel flexible rotary kilns for the cement industry. CHEC Annual Day 2009. Technical University of Denmark, Lyngby, Denmark.

4. Fuel flexible rotary kilns for the cement industry. Dansk Kemiingeniør Konference 2010, Technical University of Denmark, Lyngby, Denmark.

Participation in GS biofuel courses

Chemistry in combustion processes II. Åbo Akademi, Finland. November, 2008.

Travelling

2008:

1. Visit to Spenner Zement in Germany. Purpose: Participation in a measurement campaign of temperature and flue gas data on different locations in the preheater tower.
2. Visit to Buxton cement plant in the United Kingdom. Purpose: Raw material sampling on different locations in the preheater tower.
3. Course on Åbo Akademi, Finland. Purpose: Learn about combustion processes and ash chemistry.

2009:

1. Visit to Aalborg Portland cement plant in Denmark. Purpose: Raw material sampling on different locations in the preheater tower.
2. Several visits to FLSmidth's research center, Dania, in Denmark. Purpose: Experiments and construction of new experimental setups.
3. Participation in the Nordic Biofuels Annual Day 2009 near Trondheim, Norway.

2010:

1. Several visits to FLSmidth's research center, Dania, in Denmark. Purpose: Construction of new experimental setups.
2. Visit to Beli Izvor cement plant in Bulgaria. Purpose: Learn about their experience with alternative fuels.

References

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3. Schneider, M; Activity Report 2007-2009, Verein Deutscher Zementwerke, 2009.
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TOPIC

**Fuel flexible burners in cement and
mineral industry**

MAIN SUBJECT

Combustion of alternative fuels

SUPERVISORS

Prof., Head of Department Kim Dam-Johansen

Prof. Peter Glarborg

Assoc. Prof. Peter Arendt Jensen

PhD Morten Boberg Larsen

M.Sc.

June 2006

DOCTORAL STUDIES

Industrial PhD

Started

1st January 2009

To be completed

31st December 2011

Fuel flexible burners in cement and mineral industry

Linda Nørskov

Background

In cement production there is an increasing environmental and financial motivation for substituting fossil fuels for alternative fuels; waste and biomass. The alternative fuels introduce new challenges in the combustion processes. The present Industrial PhD project focuses on combustion of alternative fuels in the cement rotary kiln burner. Initial one-dimensional models are being developed with the aim of predicting flame properties and the possible effects on product quality, production stability, and emissions from information on physical and chemical characteristics of the fuel.

5% of the global CO₂ emissions come from the cement industry [1], of which 54% is from the limestone calcination, 34% is from fossil fuel combustion, and the remaining 12% is from the electricity consumption [2].

During the last decades an increasingly share of the fossil fuels have been substituted with alternative fuels, i.e. biofuel or waste. The substitution is mainly motivated by the following reasons:

- Low fuel cost.
- Fossil fuel resources are saved.
- The alternative fuels may be partly or fully CO₂-neutral.
- Waste is effectively utilised as energy and the ash is built into the cement product, thus no by-product are formed.

Alternative fuels cover a large range of fuels with different chemical and physical properties. The combustion process of alternative fuels may differ significant from the combustion of fossil fuel mainly due to the alternative fuels generally have larger particle sizes. Also, the alternative fuels often have a lower specific heating value due to a higher ash and moisture content. An additional challenge concerning alternative fuels is the varying and inhomogeneous physical and chemical properties resulting in a fluctuating thermal energy input.

In the typical cement plant, fuel is combusted in the calciner and in the main burner of the rotary kiln, see figure 1. At present, substitution with alternative fuels is mainly done in the calciner where larger fuel particle sizes can be accepted, hereby reducing the cost of fuel comminution.

The thermal energy for the rotary kiln is provided by a burner, introducing fuel and primary air, generating a flame into the kiln. A typical flame operating on fossil fuels has a temperature of around 2000°C to ensure proper heat transfer for the clinker formation requiring a material temperature of 1450°C [3]. The desired flame properties are generally a

relative short, narrow, stable, and centred flame with a high radiation at minimum primary air consumption and minimum formation of thermal NO_x [3]. Proper control of the combustion process and flame properties is vital for ensuring complete fuel burnout in the flame and efficient heat transfer to the clinkers to maintain process stability and clinker quality.

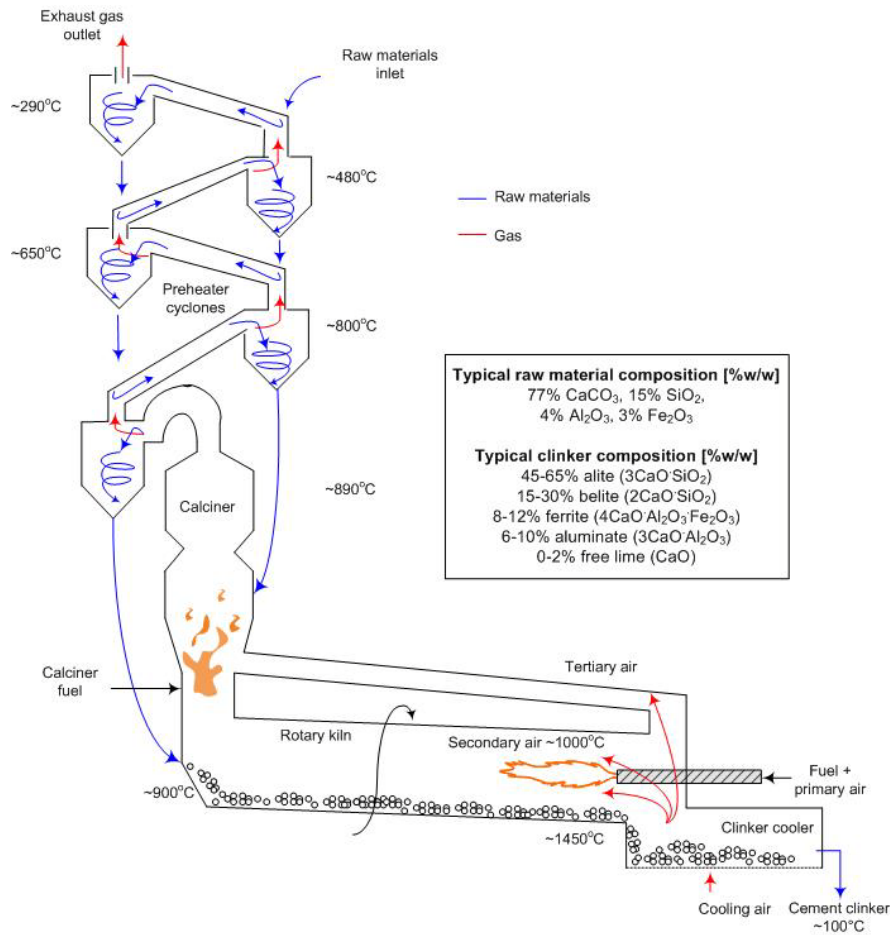


Figure 1. The pyroprocess of a cement production plant. The raw materials are preheated in a cyclone preheater tower by combustion gasses travelling countercurrent, before the calcination in the calciner unit. From the calciner the material enters the rotary kiln where it is further heated and clinkerisation reactions occur before the cement clinkers drop into the cooler unit. Hot air from the clinker cooling is used as combustion air in the rotary kiln (secondary air) and in the calciner (tertiary air).

Objectives

The main objective of this project is to develop a novel scientific framework for effective utilisation of alternative fuels in the main burner of cement and mineral rotary kilns. This will be achieved through studies of physical and chemical phenomena in the combustion process of alternative fuels in the rotary kiln and kiln burner.

The increased understanding of the combustion processes of alternative fuels will be used for optimising and redesigning fuel flexible burners and burner process settings. The goal is to develop a kiln burner that allow for

complete substitution of fossil fuels without compromising the clinker quality, production stability, and pollutant emissions.

Method

The studies involve literature studies and simplified mathematical engineering modelling. Experimental investigations in laboratories and/or pilot plants, full scale measurements at operating industrial sites are being planned.

Results

Initial one-dimensional mathematical models for the combustion process in the rotary kiln are being developed. The models should simulate the key processes and provide initial estimations of the time for complete combustion, the temperature profile in the flame, the heat transfer (radiation and convection) from the flame to the surroundings, and thermal NO formation.

The controlling parameters for the combustion process, flame formation, heat transfer and the resulting influence on the cement clinker formation will be investigated and described by mathematical models. The goal is to develop simple mathematical models of the complicated system of coupled processes occurring in the cement rotary kiln.

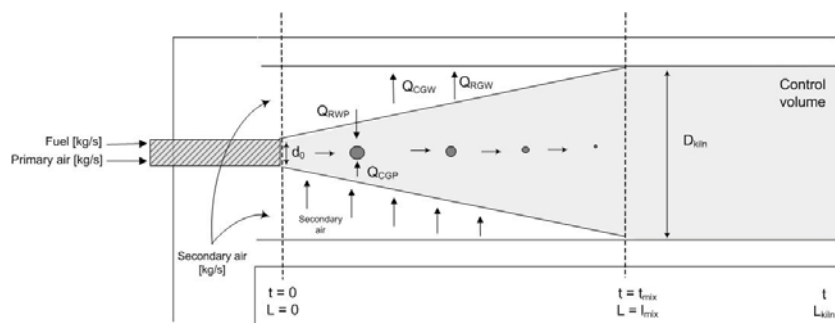


Figure 2: The model system simulating a rotary kiln flame.

Figure 1 shows a sketch of the simplified model system and control volume for the combustion calculations simulating a rotary kiln flame. Fuel particles and cold primary air is injected through a burner placed in a rotary kiln. Along the kiln length hot secondary air from cement clinker cooling is mixed into the reaction zone. The kiln length at which all secondary air is mixed into the flame is defined as L_{mix} . The fuel particles are heated by thermal radiation from the hot kiln walls. The combustion gas is heated by the energy released by combustion. In return, the hot combustion gas transfers heat to the surrounding kiln walls and the cement clinker bed mainly by thermal radiation. The model consists of coupled differential equations of gas temperature, particle temperature, and combustion rates for the specific fuel.

Figure 2 shows an example of the model calculations for combustion of polyethylene, a major component of refuse derived fuel (RDF) which is a possible alternative fuel for cement industry.

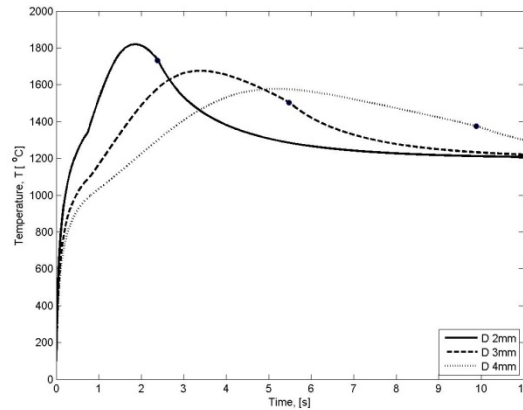


Figure 3: Gas temperature calculations as a function of time for polyethylene combustion with initial particle diameter of 2mm, 3mm, and 4mm, respectively.

One of the largest challenges of the alternative fuels compared to traditional fossil fuels is the cost of particle down-sizing. This means that the alternative fuel particles often are significantly larger than in the typical coal combustion. Figure 2 shows three gas temperature curves for three fuel particle sizes with initial diameters of 2mm, 3mm, and 4mm. The bullets in the temperature curves indicate the point where complete combustion of the individual particle size is reached. It is seen that the particle size has a significant effect on the time for complete combustion. Typical fuel residence time in a rotary kiln flame is around 2-3s and the large fuel particle may not have sufficient time for complete combustion with the present burner operation settings. This can result in ineffective heat transfer to the cement clinker charge and the unwanted situation of fuel particles falling out of the flame and continuing combustion in the cement clinker bed in the rotary kiln.

The combustion process of alternative fuel differs from combustion of fossil fuel due to different physical and chemical characteristics. Simplified mathematical models of the combustion process are being developed in the present PhD-project. It is essential that these models later in the project are validated against well-defined pilot-scale experiments, and full-scale measurements at operating cement plants.

Publications and Presentations:

Publication

Linda Nørskov, Morten Boberg Larsen, Kim Dam-Johansen, Peter Glarborg, Peter Arendt Jensen, "Fremtidens brændsler i cementindustrien", Danish Chemistry (Dansk Kemi), October, 2010

Poster

Linda Nørskov, Morten Boberg Larsen, Kim Dam-Johansen, Peter Glarborg, Peter Arendt Jensen, *Alternative fuel combustion in cement rotary kilns*, Danish Chemical Engineering Conference (DK2), 16-17th July 2010

Presentations

CHEC Annual Day, 1st Oct. 2009

Annual seminar GS-Biofuels2, 14-16th June 2009, Trondheim

Annual seminar GS-Biofuels2, 26-28th Sep. 2010, Copenhagen

Misc. internal presentations at CHEC and FLSmidth

Participation in GS biofuel courses

"Analytical techniques in combustion", CTH, NTNU, DTU, ÅÅ 2008-2009

Travelling

Annual seminar GS-Biofuels2, 26-28th Sep. 2010, Copenhagen

ECRA seminar "Kiln Firing System for Advanced Alternative Fuel Co-Firing", Opole, Poland, 29-30th June 2010

Annual seminar GS-Biofuels2, 14-16th June 2009, Trondheim Course participation "Analytical techniques in combustion", CTH 20-24th Oct. 2008, NTNU 4-7th May 2009, DTU 1-6th Feb. 2009, and ÅÅ 21-25th Sep. 2009



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TOPIC	Co-combustion of fossil fuels and waste
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MAIN SUBJECT	Ash chemistry and other ash related problems
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SUPERVISORS	Prof. Peter Glarborg Prof. Kim Dam-Johansen Assoc. Prof. Flemming J. Frandsen
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M.Sc.	August 2007
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DOCTORAL STUDIES

Started	November 2007
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To be completed	January 2011
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Co-combustion of coal and solid recovered fuel in PF-fired power plant

Hao Wu

Background

Co-combustion of coal and waste derived fuels offers a short-term and low-cost opportunity to reduce the net CO₂-emissions from dedicated coal combustion, and at the same time to get rid of a certain amount of waste produced from industry, agriculture and household. In comparison with a conventional waste incineration plant, co-combustion of coal and waste derived fuels in a pulverized coal-fired plant offers advantages such as improved electrical efficiency and higher value of usable ash products. In Denmark, the Danish government launched in February 2008 a new long term energy plan in which co-combustion of coal and waste is pointed out to give an important contribution to reduce fossil fuel consumption.

To promote co-combustion of coal and waste in Denmark, there is a need to investigate and understand the impacts of the co-combustion process and related parameters (such as coal quality, waste type and quality, waste energy fraction, particle size and injection mode) on the fuel burnout, flame stability, deposit formation and corrosion, fly ash quality, gaseous and fine particle emissions, and trace element partitions in a pulverized coal-fired plant. The results from this investigation will show whether co-combustion of coal and waste is a feasible option for pulverized coal-fired plants, and provide useful information on the optimization of waste qualities and operational parameters for the co-combustion process.

Objectives

- Identify the suitable waste quality, energy fraction and particle size that can be co-combusted in pulverized coal-fired power stations
- Investigate the influences of co-combustion on deposit formation, fly ash qualities, gaseous emission, fine particle formation, and trace element partition
- Evaluate the co-combustion process through thermodynamic modelling, especially the trace element behaviours

Method

- Performing co-combustion experiments in an entrained flow reactor with different coals, solid recovered fuels, biomass, and additives
- Conducting fine particle measurement in full-scale co-combustion of coal and solid recovered fuel
- Studying the co-pyrolysis/co-combustion characteristic of coal and waste derived materials in a lab-scale simultaneous thermogravimetric analyzer (STA)
- Investigating the release of inorganic elements during the combustion of a waste-derived fuel in a lab-scale reactor

- Using global equilibrium model to evaluate the transformation of major inorganic elements and the partition of trace elements during co-combustion of coal and solid recovered fuel

Results

Co-combustion of a bituminous coal and a solid recovered fuel (SRF) was carried out in an entrained flow reactor, and the influences of different additives including NaCl, PVC, ammonium sulphate (AmSulf), and Kaolin on co-combustion were investigated. Different SRF shares, 7.9 wt%, 14.8 wt% and 25 wt%, were applied in the co-combustion experiments, and the effects of additives on co-combustion were evaluated by maintaining the share of secondary fuel (mixture of SRF and additive) at 14.8 wt%. The experimental results showed that the fuel burnout, NO and SO₂ emissions in co-combustion of coal and SRF were decreased with increasing share of SRF. The majority of the additives inhibited the burnout, except for NaCl which seemed to have a promotion effect. The impact of additives on the NO emission was mostly not significant, except for AmSulf which significantly reduced the emission of NO. For SO₂ emission, it was found that all of the additives slightly increased the retention of sulphur in the ashes. Analysis of the bulk composition of the fly ash from different experiments indicated that the majority of the S and Cl in the fuels were released to gas phase during combustion, whereas the K and Na in the fuels were mainly retained in the ashes. During co-combustion of coal and SRF, approximately 99 wt% of K and Na in the fly ashes was present in water insoluble form i.e. as aluminosilicates or silicates. The addition of NaCl, PVC, and AmSulf generally increased the overall vaporization degree of K and Na, resulting in an increased formation of water soluble alkalis (i.e. chlorides and sulphates). Moreover, the overall vaporization degree of Na and K was found to be correlated during the experiments, suggesting an interaction between the vaporization of Na and K during pulverized fuel combustion. By collecting deposits on an air-cooled probe during the experiments, it was found that the deposition propensity of the fly ashes in co-combustion was decreased with increasing share of SRF. The addition of NaCl and PVC significantly increased the ash deposition propensity, whereas the addition of AmSulf or Kaolin showed a slight reduction effect. The chlorine content in the deposits generally implied a low corrosion potential during co-combustion of coal and SRF (up to 25 wt%), except for the experiments with NaCl or PVC addition.

Trace element behaviors in co-combustion of coal and SRF were investigated through the aforementioned experiments in the entrained flow reactor. The trace elements studied were As, Cd, Cr, Pb, Sb and Zn. The ashes from the experiments were collected as bottom ash, cyclone ash and filter ash, and were analyzed by ICP-OES. When coal was co-fired with SRF, the As, Cd, Pb, Sb and Zn contents in the filter ashes/cyclone ashes were found to increase almost linearly with their contents in the fuel ashes. This linear tendency was affected to some extent when the fuels

were mixed with the additives. The volatilities of trace elements at different experiments were assessed by using a relative enrichment (RE) factor. The results indicated that the volatilities of As, Cd, Pb, Sb and Zn were high in co-combustion of coal and SRF, whereas the volatility of Cr was relatively low. Compared with dedicated coal combustion, co-combustion of coal and SRF slightly enhanced the volatilities of Cd, Pb and Zn, but reduced the volatilities of Cr and Sb. The chlorine based additives mostly increased the volatilities of Cd, Pb and As, whereas the addition of ammonium sulphate generally decreased the volatilities of trace elements. The addition of Kaolin showed a reduction effect on the volatility of Pb, while the influences on other elements were not evident. The results from this study imply that the emission of trace elements might become a significant concern in co-combustion of coal and SRF, primarily due to the high trace element contents in the SRF. The chlorine content in the SRF as well as the sulphur and aluminosilicates contents in the coal are important parameters to control the emission of trace elements.

Fine particles formed from combustion of a bituminous coal and co-combustion of coal with 7th% (thermal percentage) solid recovered fuel (SRF) in a pulverized coal-fired power plant were sampled and characterized in this study. The particles from dedicated coal combustion and co-combustion both showed an ultrafine mode centered at approximately 0.1 μ m. Compared with coal combustion, co-combustion of coal and SRF increased the formation of submicron particles, especially ultrafine particles below 0.2 μ m. The morphology of the particles indicated that supermicron particles were primarily formed by the melting of minerals. The ultrafine particles were generated through nucleation and coagulation of vaporized inorganic species, while for the particles in between supermicron and ultrafine particles, condensation of vaporized species or aggregation of nucleates on the existing spherical submicron particles appear to be an important formation mechanism. The elemental composition of the particles from coal combustion showed that S and Ca were significantly enriched in ultrafine particles and P was also enriched considerably. However, compared with supermicron particles, the contents of Al, Si and K were depleted in ultrafine particles. The observed high volatility of Ca was attributed to the high combustion temperature and relative low oxygen condition in the boiler which may promote vaporization of Ca during char oxidation. The discrepancies on the observed volatilities of Ca and alkalis between some laboratory experiments and full-scale measurements were discussed. The composition of the fine particles from co-combustion was generally similar to those from coal combustion. The ultrafine particles from co-combustion were of slightly higher Ca, P, and K contents, and lower S content.

Besides the results mentioned above, there are some on-going work related with the PhD study, including:

- Experiments on co-firing of biomass and a waste-derived material have been performed in the entrained flow reactor. The results will be analyzed and summarized.
- Interactions between coal and some waste derived materials during the pyrolysis have been evaluated in a STA. The next step is to evaluate the synergy effects on char reactivity.
- The release of inorganic species during the combustion of a waste-derived fuel has been studied in a horizontal tube reactor and in a STA. The results were used to explain some operational problems found in an industrial plant using the same fuel. To summarize the results, a few more tests will be performed.
- Global equilibrium model is being developed to evaluate the transformation of major inorganic elements and the partition of trace elements during co-combustion of coal and SRF. The results will be compared with the experimental results from the entrained flow reactor.

The on-going work mentioned above will be summarized and included in the PhD thesis, together with the work that has already been concluded. The study plans are mostly fulfilled and some additional studies have been performed. It is aimed to submit the PhD thesis at the end of January, 2011.

Publications and Presentations:

1. H. Wu, P. Glarborg, F.J. Frandsen, K. Dam-Johansen, P.A. Jensen, B. Sander, Co-combustion of coal and SRF in an entrained flow reactor: a preliminary study, 4th European Combustion Meeting, Vienna, Austria, 2009
2. F.J. Frandsen, A.J. Pedersen, H. Wu, P. Glarborg, P.A. Jensen, O.H. Madsen, K. Lundtorp, B. Sander, Danish experiences on waste incineration on grates vs. coal-SRF co-firing in suspension, 34th International Technical Conference on Clean Coal & Fuel Systems, Florida, USA, 2009
3. H. Wu, A.J. Pedersen, P. Glarborg, F.J. Frandsen, K. Dam-Johansen, B. Sander, Aerosol formation during co-combustion of coal and solid recovered fuel in a pulverized coal-fired power plant, Joint Meeting of the Scandinavia-Nordic and French Sections of the Combustion Institute, Copenhagen, Denmark, 2009
4. H. Wu, P. Glarborg, F.J. Frandsen, K. Dam-Johansen, P.A. Jensen, B. Sander, Co-combustion of solid recovered fuel with coal in an entrained flow reactor and the effect of additives, 35th International Technical Conference on Clean Coal & Fuel Systems, Florida, USA, 2010
5. H. Wu, A.J. Pedersen, P. Glarborg, F.J. Frandsen, K. Dam-Johansen, B. Sander, Formation of fine particles in co-combustion of coal and solid recovered fuel in a pulverized coal-fired power station, Proceedings of the Combustion Institute, 33, 2010 (in press)

6. H. Wu, P. Glarborg, F.J. Frandsen, K. Dam-Johansen, P.A. Jensen, B. Sander, Behaviors of trace element in co-combustion of solid recovered fuel and coal in an entrained flow reactor, Impacts of Fuel Quality on Power Production and the Environment, Lapland, Finland, 2010
7. A.J. Pedersen, H. Wu, F.J. Frandsen, B. Sander, Combustion aerosols from cofiring of coal and solid recovered fuel in a 400 MW PF-fired power plant, Impacts of Fuel Quality on Power Production and the Environment, Lapland, Finland, 2010

Participation in GS biofuel courses

- Nordic Course in Analytical Tools in Combustion-part I, Chalmers University of Technology, Gothenburg, Sweden, 20th-24th Oct. 2008
- Nordic Course in Analytical Tools in Combustion-part II, Technical University of Denmark, Lyngby, Denmark, 2nd-6th Feb. 2009
- Nordic Course in Analytical Tools in Combustion-part III, Norwegian University of Science and Technology, Trondheim, Norway, 4th-7th May 2009
- Nordic Course in Analytical Tools in Combustion-part IV, Åbo Akademi University, Åbo, Finland, 21st-25th Sep. 2009

Travelling

- 4th UKERC Energy Summer School, 23rd-27th, London, UK
- 15th DVV Kolloquium & ToTeM 32, 15th-16th Dec. 2008, Freising, Germany
- Annual Seminar of Nordic BiofuelGS-2, 14th-16th Sep. 2008, Visby, Sweden
- Annual Seminar of Nordic BiofuelGS-2, 14th-16th Jun. 2009, Trondheim, Norway



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TOPIC	Oxy-fuel combustion
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MAIN SUBJECT	Combustion characteristics of oxy-fuel flames – Experiments and modelling
SUPERVISORS	Professor Filip Johnsson, Associate Professor Henrik Thunman
M.Sc.	February 2005
DOCTORAL STUDIES	
Started	May 2005
To be completed	Feb 2011

Combustion characteristics of oxy-fuel flames – Experiments and modelling

Stefan Hjærtstam

Background

Carbon dioxide is the dominant greenhouse gas in terms of amount of gas emitted, and global warming as a consequence of CO₂ emissions is undoubtedly one of the most challenging environmental problems of our time. Capture and storage of CO₂ produced by combustion of fossil fuels have a significant potential to contribute to CO₂ reduction, allowing for a continuous use of fossil fuels as a bridge towards more sustainable energy systems (ultimately being non-fossil). If the fossil fuel is co-fired with biomass the contribution of the reduction could be even greater. Oxy-fuel combustion (also known as O₂/CO₂ combustion) is emerging as a possible carbon-capture technology, due to its comparatively favorable economics, and since it is more or less based on known technology. In oxy-fuel combustion, N₂ is separated from the air, and the fuel is burnt in a mixture of O₂ and recycled flue gas. The resulting high concentration of CO₂ in the flue gas enables direct CO₂ recovery. If a mixture of fossil fuel and biofuel is co-fired in a future oxy-fuel power plant, a negative (or zero) contribution of CO₂ to the atmosphere is possible, if the emitted CO₂ is captured and stored. Recent research has shown that the combustion properties of oxy-fuel flames differ from those of conventional air-firing. Oxy-fuel flames often possess high in flame concentrations of CO, but the emission levels of CO are often comparable with the emissions of conventional combustion.

Computational fluid dynamics (CFD) is a modelling tool used within industry and research to simulate both non-reacting and reacting flows. Combustion models, incorporated in CFD software, are commonly aimed and tuned for traditional combustion using air to oxidize the fuel. Due to the different oxidant composition in oxy-fuel combustion compared to in air-firing, there is a general need and interest to further develop the present CFD-tools to better predict oxy-fuel combustion environments.

Objectives

1. Investigate the influence of different O₂ fractions (recycle rates) in the feed gas during oxy-fuel combustion and compare the results with a reference air-fired case. Objective completed in 2007.
2. Examine the effects on the flame structure and the emissions that follow from changing the recycle rate in oxy-fuel combustion. With the aim to gain sufficient data for future modelling of oxy-fuel flames. Objective completed in 2008.
3. Evaluate the ability of existing turbulence and chemistry models in CFD to handle oxy-fuel combustion. Objective completed in 2009.

4. Investigate the performance of global reaction mechanisms developed for oxy-fuel conditions. Objective to be completed in 2010.
5. Evaluate gas radiation models suitable oxy-fuel conditions using CFD. Objective to be completed in 2010.

Method

In 2007 measurements of temperature, gas composition and radiation intensity in Chalmers 100 kW combustion unit for three different oxy-fuel cases, in terms of O₂ concentration in the feed gas, were performed and compared with a reference air-fired case.

Computational fluid dynamics have been used to model propane-fired oxy-fuel combustion in the Chalmers 100 kW unit. The influence of the choice of turbulence model in combination with suitable global reaction mechanisms have been investigated to set up a base line case for future modelling of oxy-fuel flames. Different global reaction mechanisms specifically developed for oxy-fuel conditions have been investigated and compared with common global mechanisms developed for air-fired conditions.

Models for treating the radiative properties of gaseous oxy-fuel flames have been evaluated using CFD and theoretical calculations (Matlab). The impact of soot radiation was also investigated.

Results

- The combustion characteristics of oxy-fuel flames have been investigated experimentally. The replacement of N₂ with mostly CO₂ that follows with oxy-fuel conditions has consequences on the combustion characteristics. A higher O₂ fraction in the feed gas is needed if air-fired temperatures are to be reached, typically 25-30 vol % O₂ instead of 21 vol % (as in air) depending on the fuel used. The concentration of CO during oxy-fuel combustion might be high within the actual flame at high temperatures due to the water-gas shift reaction. However, controlling the emission of CO in the stack gas is not necessarily more problematic than during air-firing, since the burnout still is sufficient.
- Three turbulence models (the standard k-e model, the Realizable k-e model and the Reynolds stress model) have been evaluated in CFD. The choice of turbulence model has a large impact on the final result, in terms of flow pattern, temperature distribution and gas composition. Nevertheless, the same model specific tendencies were exhibited during both oxy-fuel and air-firing. Hence, there is a general need, not only in connection to oxy-fuel, for more accurate turbulence models. These model need to be simple enough to give a reasonable computational effort.
- In the evaluation of air-derived global reaction mechanisms, the Jones and Lindstedt (JL) mechanism gave promising results when modelling oxy-fuel flames. The model was able to capture the

measured trends in terms of temperature and gas composition for an oxy-fuel flame. However, three global reaction mechanisms derived for oxy-fuel conditions have also been evaluated using CFD. All three mechanisms yield and improved prediction of CO in the flame compared to the JL mechanism.

- A non-gray version of the Weighted-Sum-of-Gray-Gas model, derived for oxy-fuel conditions, have been evaluated using CFD and theoretical calculations. The results showed that a non-gray approach gives a better description of the radiative properties than a traditional gray approach. Soot radiation were also evaluated and found to be of large importance for the CFD result.

The experimental part of the PhD-studies was initially aimed to be a small part of the work. The focus of the work was mainly aimed to be on CFD-modelling of oxy-fuel combustion. However, due to time consuming complications in the experiments and parental leave the PhD-period was prolonged until February 2011.

Publications and Presentations:

1. Hjærtstam, S., Andersson, K., Johnsson, F. Combustion characteristics of lignite-fired oxy-fuel flames. Presentation and extended abstract - The Proceedings of the 32nd International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, Florida, USA, June 10-15, 2007.
2. Andersson, K., Johansson, R., Hjærtstam, S., Johnsson, F., Leckner, B. Radiation intensity of lignite-fired oxy-fuel flames. *Experimental Thermal and Fluid Science*, Volume 33, Issue 1, Pages 67-76, 2008.
3. Hjærtstam, S., Andersson, K., Johnsson, F. Combustion characteristics of lignite-fired oxy-fuel flames. *Fuel* 88: 2216-2224, 2009.
4. Hjærtstam, S., Johansson, R., Andersson, K., Johnsson, F. Evaluation of gas radiation modeling in oxy-fired furnaces. Presentation and extended abstract - AIChE, 2010 Annual Meeting, Salt Lake City, UTAH, USA, November 7-12, 2010.
5. Hjærtstam, S., Normann, F., Andersson, K., Johnsson, F. Performance of global reaction mechanisms in oxy-fuel conditions. (To be submitted for publication 2010)
6. Hjærtstam, S., Johansson, R., Andersson, K., Johnsson, F. Evaluation of gas radiation modeling in oxy-fired furnaces. (To be submitted for publication 2010)

Participation in GS biofuel courses

- Thermo chemical conversion of biomass and waste (2007). Chalmers University of Technology.
- Analytical Techniques in Combustion:
 - Part 1: Chalmers University of Technology, Gothenburg October 20 – 24 2008

- Part 2: Technical University of Denmark, Copenhagen
February 2 – 6 2009
- Part 3: Norwegian University of Science and Technology,
Trondheim May 4 – 7 2009

-

Travelling

Annual meetings:

- BiofuelsGS-2 Annual Meeting, Turku, Finland, September 2007.
- BiofuelsGS-2 Annual Meeting, Visby, Sweden, September 2008.

Courses:

- Analytical Techniques in Combustion, Part 2: Technical University of Denmark, Copenhagen, February 2-6 2009.
- Analytical Techniques in Combustion, Part 3: Norwegian University of Science and Technology, Trondheim, May 4-7 2009.

TOPIC	Fixed-bed combustion
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MAIN SUBJECT	Modeling of combustion of biofuels in grate furnaces
SUPERVISORS	Assistant Professor Henrik Thunman Professor Filip Johnsson
M.Sc.	2004
DOCTORAL STUDIES	
Started	2004
Completed	2010

Modeling of combustion of biofuels in grate furnaces

Sven Hermansson

Background

The use of biofuels for production of heat and power has increased during the last decades. One of the most frequently used techniques for conversion of biofuels into energy is combustion in grate furnaces. Grate furnaces are typically installed in small scale power plants, i.e. plants with production capacity under 40 MW_{th}, because of their benefit in simplicity concerning construction and control systems compared to e.g. fluidized bed boilers. In Sweden there exist around 350 grate furnaces for production of 40 MW_{th} and more, and many more at lower capacities.

The design of grate furnaces, especially the small scale ones, is much dependent upon practical experience. Creating combustion models, both for the conversion in the fuel bed and in the gaseous phase, could give the furnace developers a useful tool for improvement of not only the efficiency and emissions of the furnace but also increasing the flexibility in the use of fuels and avoiding grate-material deterioration.

Today, the available bed-combustion models for engineering studies of grate furnaces are very simplified. When visually studying the combustion in a grate furnace it can be seen that there exists a range of effects that differ from the idealized view of the combustion and that need to be taken into account to create a reliable model. Such effects are e.g. channeling inside the fuel bed and at the bounding walls which are suspected to cause elevated emission levels of harmful substances. An increasing problem in grate furnaces that puzzles the users is, also, grate deterioration. To some extent the disturbances and deterioration can be explained by practical issues like insufficient fuel mixing and air maldistribution through the fuel bed, but there are still a range of uncertainties that need to be further investigated. Therefore it is seen as important to develop models for the combustion that can take these multidimensional effects in the fuel bed into account. The models should thereafter be implemented into engineering CFD-models that describe the real combustion situation in grate furnace.

Objectives

6. Expanding a two-dimensional isothermal model of fixed bed combustion in a commercial CFD-software (developed during biofuelsGS-1) to include non-isothermal conditions.
7. Analyzing with CFD-modeling channelling flow inside a fixed fuel-bed and at the presence of a solid wall.
8. Analyzing with CFD-modeling the influence of grate and air-flow configuration as possible causes to grate-material deterioration.
9. Introducing theories of non-linear bed shrinkage and fuel flow due to conversion.

Method

CFD with existing models of thermal conversion of solid fuel, complemented with own theories of bed shrinkage and movements.

Results

- The 2D CFD model of fixed-bed combustion has been expanded to describe also non-isothermal conditions.
- Influence from heterogeneous conditions on the conversion of fuel beds, applicable to combustion in grate furnaces have been investigated with the CFD-model. Major results are that large porous variations inside the fuel bed have potential to cause channels to grow up through the fuel bed, while the porous jump that naturally is caused by the imperfection in the packing of fuel particles towards a wall only will give rise to fluctuations in the conversion close to the grate.
- Influence from grate-configuration (air-hole distribution and flue-gas recirculation) on the grate temperature and oxygen concentration along the grate has been investigated with the CFD-model. To avoid extreme temperatures in the grate and consequent material deterioration, grates should be designed so that the entering velocity of the air to the fuel bed becomes high. This could be achieved by reducing the number of holes in the grate rods. The holes should, though, not be outplaced at distances exceeding 4-5 cm to avoid reducing conditions and carburizing corrosion of the grate-material. To reduce the thermal load of the grate and at the same time maintain oxidizing conditions at the grate surface, flue-gas recirculation was found to be an efficient measure.
- Theories of non-linear bed-shrinkage and fuel-flow in fixed-bed combustion have been developed from a laboratory combustion experiment. The experiment shows that bed shrinkage due to the conversion is a combination of continuous shrinkage and distinct bed collapses. The collapses are believed to be caused by build-up of porous structures during the conversion, which finally implode. A model of this procedure is implemented into the CFD model and the simulation results agree well with the shrinkage behaviour of the fuel bed in the laboratory experiment.
- During the period of biofuelsGS-2, an additional objective was formed. To control the combustion in grate furnaces that burn wet fuels, it is of importance to continuously monitor the moisture content of the fuel. So far, there has been no method to directly measure the moisture content of the fuel or indirectly determine it from flue-gas measurements that, at the same time, is economically feasible for combustion units of the typical size of grate furnaces. Here, an alternative method for indirect determination of the moisture content of the fuel was developed. The relative humidity of the flue gases was measured with a sensor-equipment that is less costly than other existing methods. The results show that the method responds within seconds to changes in the moisture content

of the furnace flue gases, which means that it can be used to control both the fuel feed and the combustion air. Furthermore, the method can be used to determine the level of moisture-content of the fuel in the furnace with high accuracy (< 3% error), if calibration is performed with a fuel of known moisture content.

Due to unexpected complications with the measurement campaign, the PhD-period was prolonged. End of period is preliminary set to December 2010. As writing, date for dissertation is discussed with opponent.

Publications and Presentations:

1. Hermansson, Sven; Thunman, Henrik: Two-dimensional CFD-modeling of multi-particle scale phenomena in fixed bed combustion. (To be submitted during October 2010)
2. Hermansson, Sven; Thunman, Henrik: Grate design and operational measures to reduce grate-material wear in fixed-bed combustion. (To be submitted during October 2010)
3. Hermansson, Sven; Lind, Fredrik; Åmand, Lars-Erik; Thunman, Henrik: On-line monitoring of the fuel moisture-content in biomass-fired furnaces by measuring the relative humidity of the flue gases. (To be submitted during October 2010)
4. Hermansson, Sven; Brink, Anders; Thunman, Henrik: Structural collapses and inhomogeneous flow conditions in fixed-bed combustion. Proceedings of the American-Japanese Flame Research Committees International Symposium, 2007
5. Frigerio, Simone; Thunman, Henrik; Leckner, Bo; Hermansson, Sven: Estimation of gas phase mixing in packed beds. *Combustion and Flame*, 153 pp. 137-148, 2007
6. Hermansson, S.: 'Disturbances in Fixed-Bed Combustion', *Thesis for Degree of Licentiate of Engineering*, Chalmers University of Technology, Göteborg, Sweden, 2007.

Participation in GS biofuel courses

-

Travelling

Exchange visit to Åbo Akademi University, Turku, Finland, September-December 2007,
BiofuelsGS-2 Annual Meeting, Turku, Finland, September 2007,
IFRF American-Japanese Flame Research Committees International Conference + 30th TOTeM30, Waikoloa Beach, USA, 22th-26th October 2007,
Exchange visit to Åbo Akademi University, Turku, Finland, 12th-13th September 2008,
BiofuelsGS-2 Annual Meeting, Visby, Sweden, September 2008,
BiofuelsGS-2 Annual Meeting, Trondheim, Norway, June 2009,
BiofuelsGS-2 Annual Meeting, Copenhagen, Denmark, September 2010.



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TOPIC **Biomass gasification**

MAIN SUBJECT **Tar cleaning and gas conditioning**

SUPERVISORS Professor Henrik Thunman
Dr Martin Seemann

M.Sc. **Chemical Engineering 2008**

DOCTORAL STUDIES

Started October 2008

To be completed October 2013

Continuous tar cleaning with simultaneous catalyst regeneration in a dual fluidised bed reactor

Fredrik Lind

Background

Gasification is recognized as an effective route for converting the heterogeneous bound energy within lignocelluloses to a gaseous fuel. However, in addition to the major produced gas components (H_2 , CO , CO_2 , CH_4 , H_2O and light hydrocarbons) the raw gas generally contains unacceptable amounts of condensable hydrocarbons (referred to as tars). The tar components are associated with operational problems such as clogging and blockage of equipment downstream the gasifier. The tar components also preclude the direct use of producer gas in internal combustion engines and gas turbines. Consequently, upgrading the raw gas to a gaseous fuel or to a primary gas suitable for liquid fuel production has to involve gas cleaning.

Hot gas cleaning is usually preferred in prior to techniques for wet cleaning, as the wet cleaning is associated with large quantities of waste water/solvents and thermodynamic penalties coupled to the condensation of the tars. At present, primary and secondary techniques associated with catalytic tar reforming are seen as the most promising hot gas cleaning methods. However, a major drawback with catalytic tar cleaning is that the catalyst rapidly becomes deactivated by carbon deposits on the active surfaces.

We have developed a novel technique for continuous catalytic tar removal with simultaneous regeneration of the catalysts. The tar cleaning principle is based on the technique for chemical looping reforming (CLR). The reactor system utilizes a circulating metal oxide (MeO) as oxygen supplier and heat carrier for partial oxidation of the tar components into CO and H_2 . In this manner the producer gas is not diluted with nitrogen, since, direct contact between the producer gas and the air is avoided.

The reactor system has two reactors, one for air and one for the tar containing producer gas, Fig 1. Two loop seals (LS), fluidised with inert gas or steam, prevent gas leakage but enables the catalyst to circulate between the two reactors. The MeO is reduced to Me during the partial oxidation of the tar components in the reformer (FR) according to reaction (1). Reducing the MeO to Me is, depending on the oxygen carrier, usually an endothermic reaction. Besides the desired tar reforming reaction additional carbon forming reactions cause coke deposits on the Me. Simultaneously as the Me is re-oxidized to MeO in the regenerator (AR) the coke deposits on the catalytic surfaces is oxidized to CO_2 according to reaction (2). The re-oxidation of the Me to MeO is strongly exothermic.

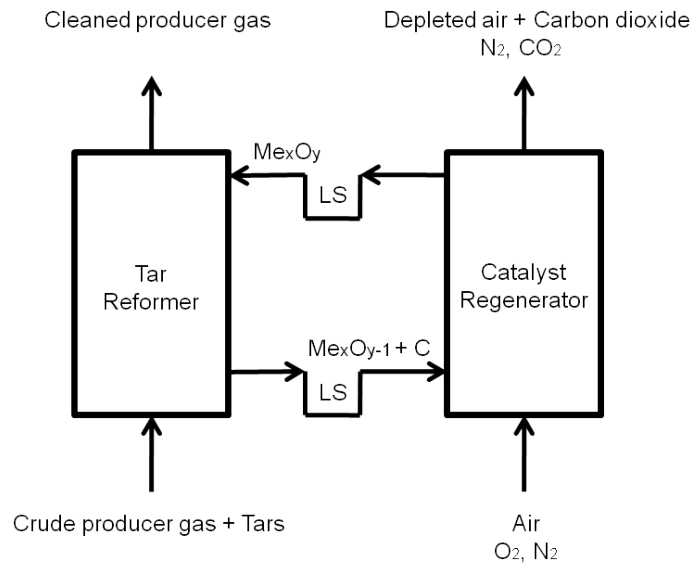
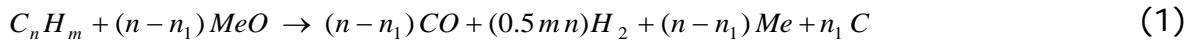
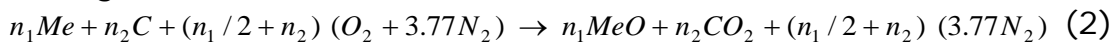


Figure 1 Dual fluidised bed system for tar removal with circulating catalyst/oxygen-carrier

Partial oxidation of tars with coke formation on catalyst surfaces:



Me regeneration and oxidation:



Objectives

1. Literature studies and development of an analysis system for the raw gas from the gasifier.
2. Examine the composition of the raw gas when using different fuel and different operation conditions in the gasifier.
3. Study tar cleaning technologies and develop a method for tar cleaning and tar utilization.
4. Optimization of the concept to reach product gas with preferable tar composition
5. Investigate the potential for scaling the tar cleaning concept suitable for industrial purposes

Method

1. Building up a gas analysis system by using chemical- and mechanical engineering. The system should include gas cooling and cleaning as well as the analysing equipment, e.g. gas chromatography.
2. The components in the raw gas are determined in the gas analysis system.
3. Building up a tar cleaning/utilisation system with catalysts in interconnecting fluidised beds.
4. Optimization by combining effects from changing temperatures, different catalysts and oxygen transfer
5. Collaboration with the division of Heat and Power Technology

Results

The gasifier was taken into operation during 2007 and the gas analyzing system was operational in 2008. During 2009 the gas analysis system was improved and the CLR system was built. The tar cleaning and regeneration concept was evaluated during spring 2010 by using a mix of ilmenite (FeTiO_3), 60 % by mass, and silica-sand, 40 % by mass, as bed material. Raw gas from the gasifier was fed to the reformer reactor and the CLR system was operated at 700, 750, 800 °C. Figure 2 show the tar content in the feed to the CLR (reference) and the tar content leaving the CLR for the 3 temperatures. Low tar reforming activity is observed at 700 °C. One explanation for the low activity can be coupled to the crude catalyst material, which needs to be activated during cycles of oxidizing and reducing conditions to reach full activity. At 700 and 800 °C the total amount of tars was decreased by 35 and 55 % respectively.

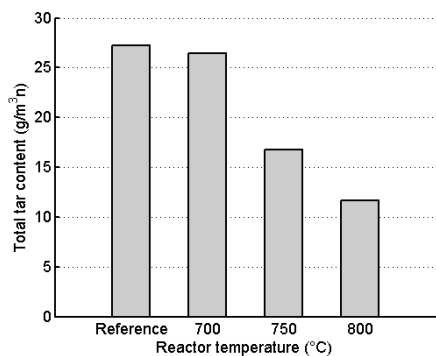


Figure 2 Total tar content in and out of the CLR system

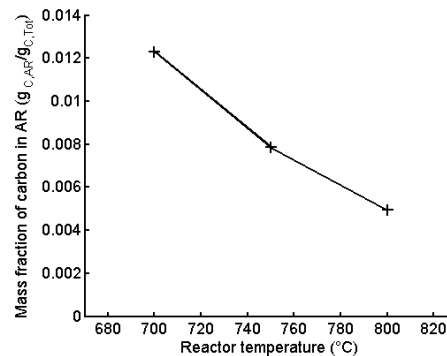


Figure 3 Carbon fraction in AR

The CO_2 , CO and O_2 content in the outlet of the regenerator was sampled each second during the experiment. Only CO_2 was detected during the regeneration cycle. Figure 3 illustrates the carbon fraction that is transported, as carbon deposits on the catalytic surfaces, from the reformer to the regenerator. As much as 1.2 % of the total amount of feed carbon to the system ends up as carbon deposits on the catalyst in the FR at 700 °C. It is obvious that an increase in temperature decreases the amount of carbon deposits and at 800 °C the carbon transport was decreased to 0.5 %. The CO_2 measurements together with the tar sampling show that the proposed concept of tar cleaning with simultaneous catalyst regeneration is working.

Future experiments will be focused on reaching more efficient tar conversion. The strategy is to evaluate effects from changing the temperature conditions together with different catalysts and controlling the amount of transported oxygen.

An investigation of the possibilities to scale the CLR system suitable for industrial purposes will be performed. The strategy is to use gained data

from CLR experiments in a flow sheeting software in collaboration with the division of Heat and Power Technology.

Publications and Presentations:

Henrik Thunman, Fredrik Lind, Filip Johnsson. Inventering av framtidens el- och värmeproduktionstekniker, Delrapport Energikombinat (Elforsk nr 08:79) 2008.

Fredrik Lind, Martin Seemann, Henrik Thunman. Evaluation of fluid dynamics in a hot and a cold system of interconnecting fluidised beds. In International conference on fluidization, Fluidization XIII, Gyeong-ju Korea, 2010; pp 869-876.

Sven Hermansson, Fredrik Lind, Lars-Erik Åmand, Henrik Thunman. On-line monitoring of fuel moisture-content in biomass furnaces by measuring relative humidity of the flue gases. To be submitted for publication in 2010

Fredrik Lind, Martin Seemann, Henrik Thunman. A dual fluidised bed reactor for continuous catalytic tar reforming and catalyst regeneration. To be submitted for publication in 2010

Fredrik Lind, Martin Seemann, Henrik Thunman. Evaluation of fluid dynamics in a hot and a cold system of interconnecting fluidised beds. Extended abstract and oral presentation, Joint meeting of the Scandinavian and French Section of the Combustion Institute. Copenhagen, 9 – 10 November 2009.

Fredrik Lind, Martin Seemann, Henrik Thunman. Experiences from recent tests in an interconnecting fluidized bed Oral presentation at the 60th IEA-FBC Technical Meeting at Chalmers University of Technology Gothenburg May 3 – 4 2001.

Fredrik Lind, Martin Seemann, Henrik Thunman. Evaluation of fluid dynamics in a hot and a cold system of interconnecting fluidised beds. Poster and oral presentation, In International conference on fluidization, Fluidization XIII, Gyeong-ju Korea May 16 – 21, 2010.

Participation in GS biofuel courses

- Thermo chemical conversion of biomass and waste (2007). Chalmers University of Technology.

Analytical Techniques in Combustion:

- Part 1: Chalmers University of Technology, Gothenburg October 20 – 24 2008
- Part 2: Technical University of Denmark, Copenhagen February 2 – 6 2009
- Part 3: Norwegian University of Science and Technology, Trondheim May 4 – 7 2009

Travelling

Annual meetings (performed):

- Visby, September 14 – 16 2008. Flight to Visby from Gothenburg via Stockholm. Flight to Gothenburg from Visby via Stockholm.
- Trondheim, June 14 – 16 2009. Flight to Trondheim from Gothenburg via Oslo. Flight to Gothenburg via Oslo.

Annual meetings (coming up):

- Copenhagen, September 26 – 28. Train from Gothenburg to Copenhagen. Train to Gothenburg from Copenhagen.

Analytical Techniques in Combustion:

- Part 2: Technical University of Denmark, Copenhagen
February 2 – 6 2009. Train from Gothenburg to Copenhagen.
Train from Copenhagen to Gothenburg.
- Part 3: Norwegian University of Science and Technology,
Trondheim May 4 – 7 2009. Flight to Trondheim from
Gothenburg via Oslo. Flight to Oslo and then train back to
Gothenburg.

TOPIC	Fluidized bed combustion
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MAIN SUBJECT	Waste combustion in fluidized beds
SUPERVISORS	Professor Henrik Thunman Dr David Pallarès
M.Sc.	Chemical Engineering 2008
DOCTORAL STUDIES	
Started	Nov 2008
To be completed	Nov 2013

Fluidized bed combustion – fuel dispersion and bubble flow distribution

Johanna Olsson

Background

Fluidized bed (FB) boilers are widely used for biomass and waste combustion, two fuels with high contents of volatiles. For economy-efficiency reasons, large boiler units are preferable but boilers with large cross sectional areas often experience problems distributing the fuel evenly in the bed. Fuel entering a FB boiler release a large amount of combustible gases (devolatilizes) into the freeboard, leaving the solid char in the bed. Rapid devolatilization can create a maldistribution of combustibles in the furnace, unfavorable for the performance of the boiler since the maldistribution not only affects the combustion degree but also the heat profile and the formation of emissions. The boilers performance strongly depends on fuel-gas contact, thus, a large cross-sectional area makes the boiler more sensitive to the fuel mixing and gas distribution.

Solids mixing rates in large-scale FB units are higher in the vertical than in the lateral direction and, thus, the latter being critical for the overall fuel mixing since the bed height to width ratio (aspect ratio) often are around 1 or lower in boilers. Important for modeling and scale up of FB boilers is the ratio between the characteristic times for horizontal fuel dispersion and fuel conversion. It has since long been accepted that solids (including fuel) mixing in FBs is induced and governed by the bubble flow. At operational conditions representative to those in boilers the fuel flow pattern is structured in horizontally-aligned vortices induced by the formation of stable bubble paths through the bed. Bubble paths form due to the low-pressure paths created when bubbles rising through the bed are followed by other bubbles. The formation of bubble paths results in an uneven lateral bubble flow distribution. The bubble flow properties are governed by the operational conditions and in order to be able to improve FB boiler performance it is important to understand the influence of operational conditions on the bubble flow and on the fuel mixing mechanism.

To a large extent, the bubble flow also determines the distribution of oxygen in the furnace. Boilers operate at fluidization velocities far higher than minimum fluidization and with low gas distributor pressure drops which promotes large bubbles of an exploding type. The gas flow is considerably higher than what corresponds to the visual bubble flow and a significant fraction of the gas flow passes the dense bed as so-called throughflow following the bubble paths. Thus, there is a clear and strong correlation between the fuel mixing mechanism and the bubble flow distribution. However, no correlation between the lateral bubble flow distribution and fuel mixing pattern in large scale FB boilers is available.

Objectives

1. Literature survey of available investigations and models for fuel mixing and bubble flow distribution in large scale units.
2. Investigation of the influence of operational conditions on the bubble flow distribution in a 2D cold model and.
3. Investigation of the fuel mixing mechanism in a large scale fluidized bed unit.

Method

1. Investigate the bubble flow distributions dependency on operational conditions in a 2D cold model.
2. Develop and test a method for real time tracking of the fuel mixing process under normal operation in a large scale unit
3. Investigate fuel mixing mechanism in a large scale fluidized unit under cold conditions

Results

A digital image analysis (DIA) method has been used to study the influence of operational parameters on the lateral bubble flow distribution in a cold 2D fluidized bed model. The bubble distribution profile (Fig. 1) obtained for four different cases show that the operational conditions have a strong impact on the lateral bubble flow distribution. The evenness in the bubble flow distribution is measured as the variance of the distribution profile (Fig. 2) which decreases with increasing gas velocity or bed height and, to a smaller extent, increasing gas distributor pressure drop. A low variance indicate an even bubble distribution but is no guarantee that the entire bed is fluidized properly.

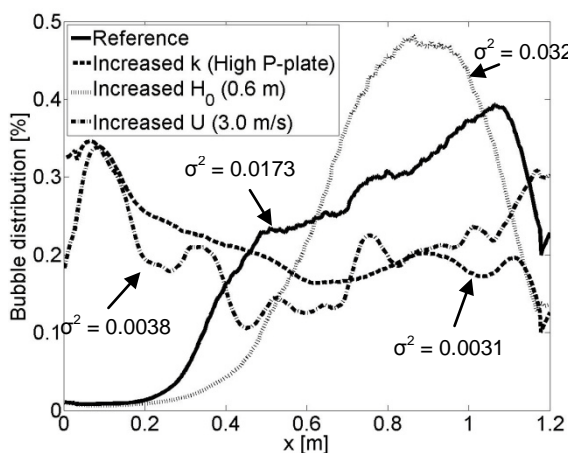


Figure 1: Bubble distribution profile as obtained from DIA. Reference conditions: Low Δp -plate, $H_0 = 0.2$ m and $u = 0.75$ m/s.

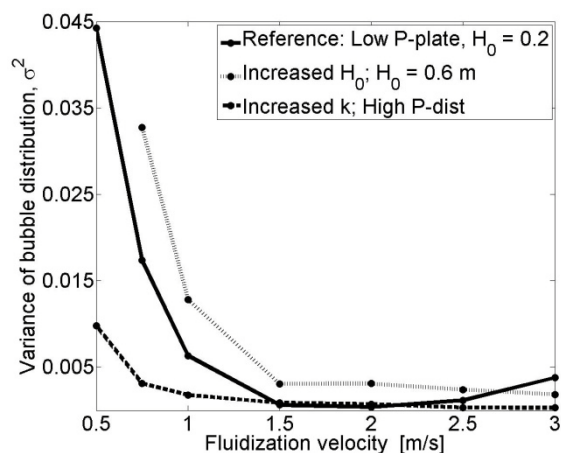
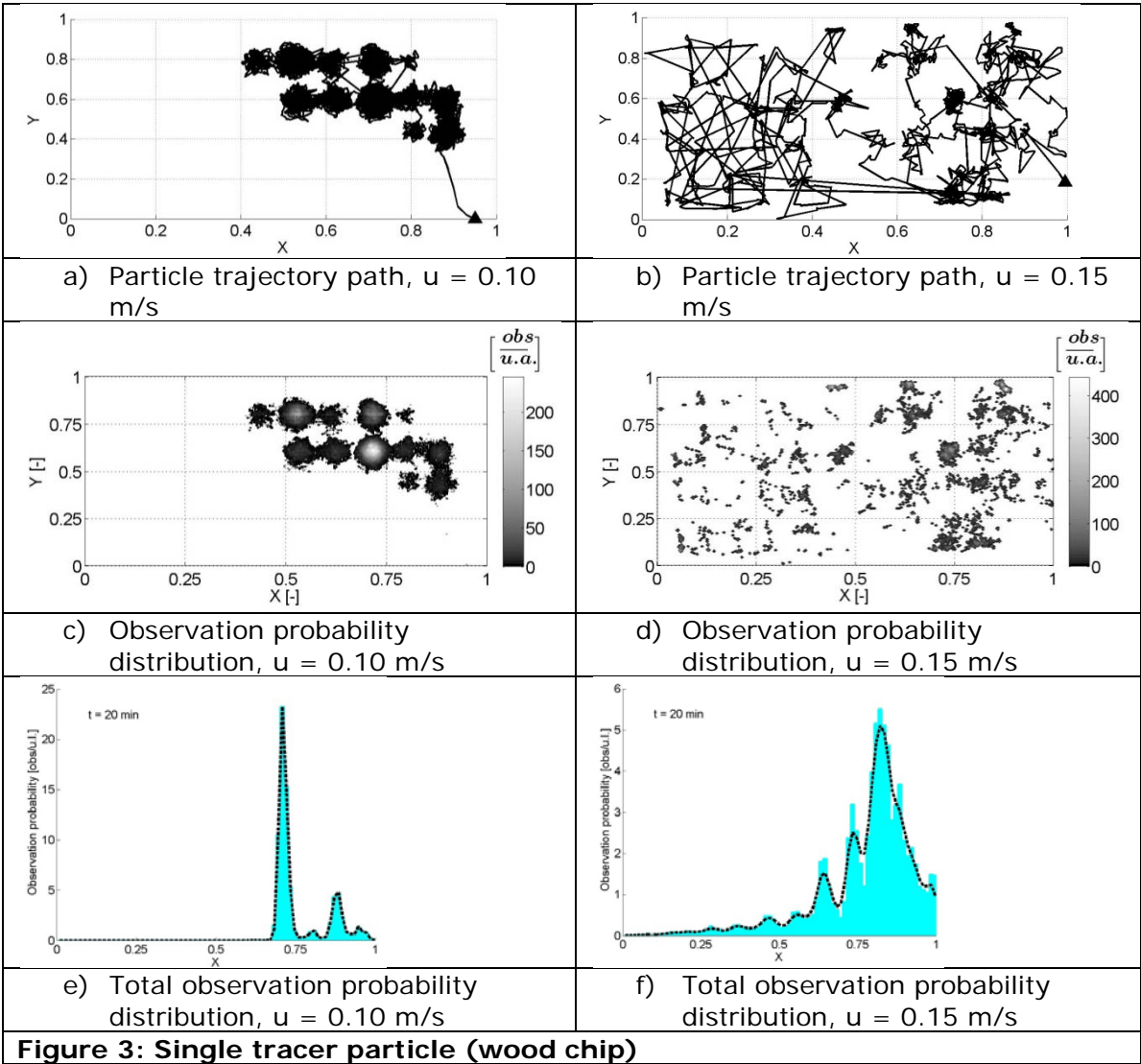


Figure 2: Variance of bubble flow profile as a function of fluidization velocity. Reference conditions: Low Δp -plate and $H_0 = 0.2$ m.

The horizontal bubble distribution depends, as can be seen in Fig. 1-2, on all three investigated key parameters. For any combination of dense bed height and gas distributor plate there is a certain gas velocity above which

the lateral bubble distribution becomes even which is determined by the ratio between the pressure drop across the distributor and the bed. However, due to operational costs, the gas distributor pressure drop is often kept as low as possible.

The fuel mixing mechanism has been investigated in a large-scale fluidized bed operated under cold conditions through particle tracking techniques and DIA for both single and batches of fuel tracer particles. The trajectory of a single particle on the surface of the fluidized bed can be mapped (Fig. 3a-b) when connecting subsequent observations.



Although both the lower ($u = 0.10$ m/s) and the higher ($u = 0.15$ m/s) velocity fluidize the bed entirely; the tracer particle gets stuck between the nozzles at the lower velocity, while this tendency is much alleviated at the higher velocity, Fig. 3a-d. The local variations in tracer observation probability profile (Fig. 3e-f) indicate that the bubble paths formed above the nozzles create a local variation at the meso-scale which is averaged out at the macro-scale when estimating the dispersion of the tracer with

diffusion like transport. At both gas velocities, the tracer particle spend on average more time on the bed surface than in the bed. However, it is important to point out that at the low velocity the transport of the particle takes place mostly in the bed while on the bed for the higher velocity.

The tracer particles traceability decreases during the experiment (Fig. 4) which results in difficulties in determining the particles position and in collecting sufficient observations to ensure statistical reliability. The obvious result from these experiments is that the lateral fuel mixing rate is not high enough for the tracer to traverse the entire length of the bed while the tracer is observable, which is on average 30 min (Fig 5a-c). The random movement of a single tracer particle combined with the limited traceability results in a statistical uncertainty in collected data but batches provide more statistically reliable data. Hence, also the dispersion of a batch of tracer particles has been investigated.

For a batch of particles the dispersion coefficient can be estimated with Einstein's equation:

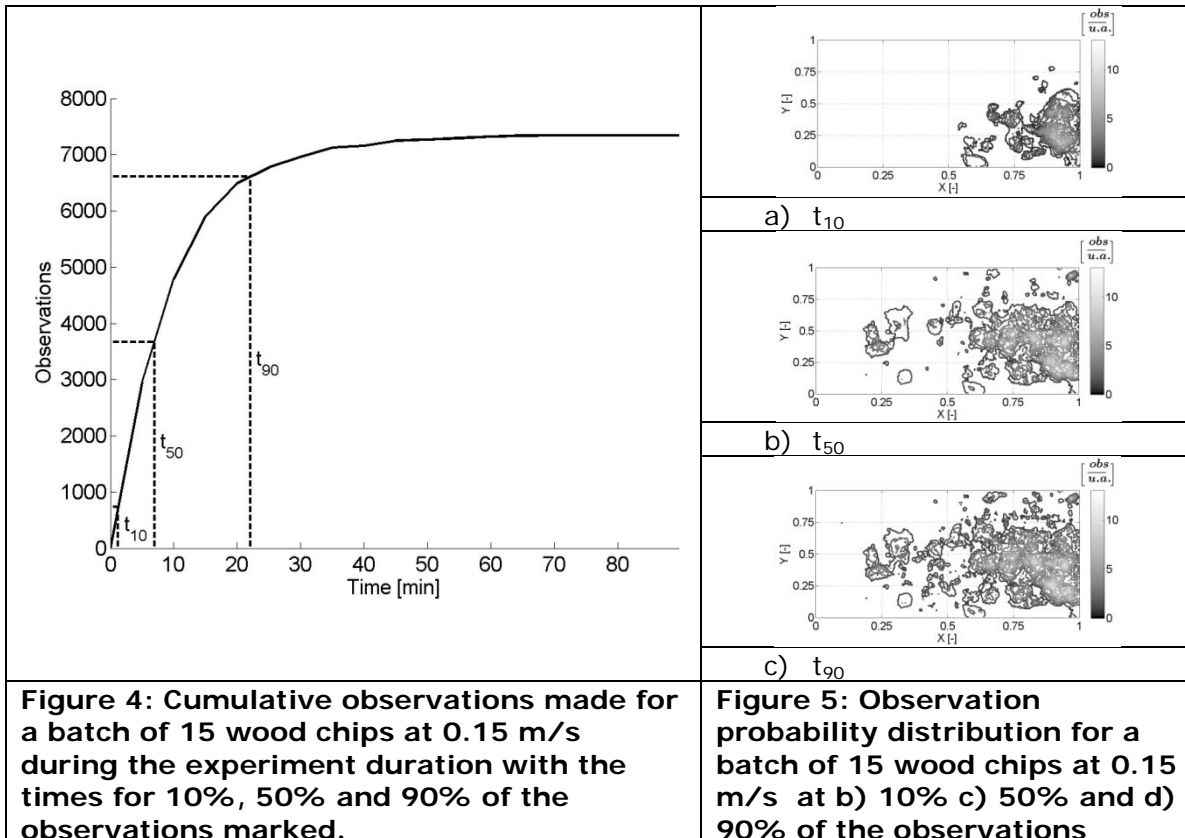
$$D_k = \frac{\sum_{i=1}^N \left(\frac{\Delta L_n^2}{2\Delta t} \right)_i}{N} \quad (1) \quad k = x, y, \text{ or } L$$

where

N = Number of tracer particles

ΔL_n = net displacement for particle i , in the k direction

Δt = time elapsed between start and present



Since the particles cannot be traced continuously (only visible on the bed surface) and the tracking technique doesn't allow for identification of single particles close together, the calculation of the dispersion coefficient is based on a modified version of Einstein's equation. The bed surface is divided into mixing cells, based on the nozzle arrangement and the concentration of the tracer particles is obtained based on the illuminated pixels in each frame. The illuminated cells at each observation are used to calculate the lateral fuel dispersion coefficient as a function elapsed experimental time (Fig 6a). The global dispersion coefficients given in Table 1 are derived through averaging the period between the times at which 10% and 50% of the total amount of observations has made or the time the particles reach the wall, i.e. between t_{10} - t_{50} or t_{10} - t_x and t_{10} - t_y , respectively (Fig 6b).

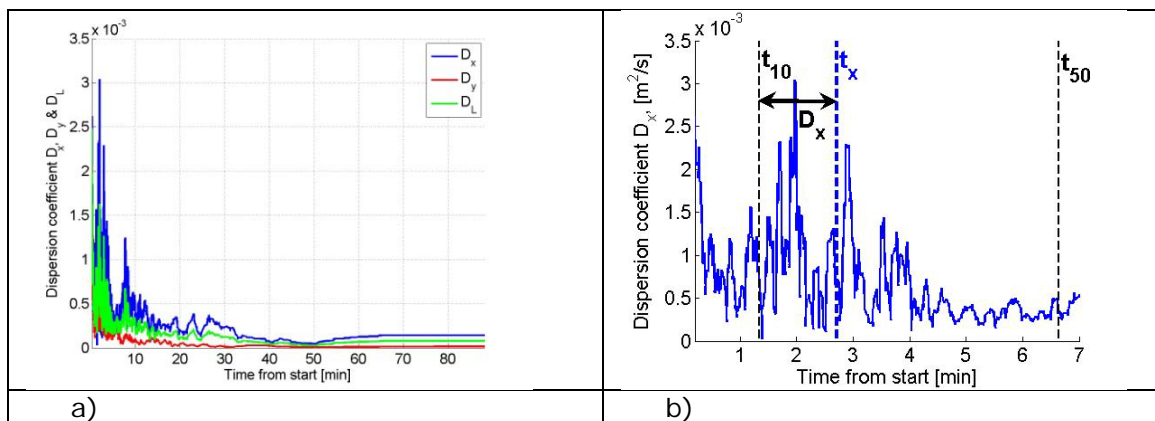


Figure 6: Lateral dispersion coefficient as a function of elapsed experimental time. a) D_x , D_y and D_L for a batch of 15 wood chips at $u = 0.15 \text{ m/s}$, b) Variation of D_x during time interval 0.02 – 7.00 min with the times for t_{10} , t_x (the particles reach the wall in the x-direction) and t_{50} and the interval for estimating D_x in this case marked

Table 1: Dispersion coefficient for the different cases

Fuel	0.10 m/s		0.15 m/s				
	Wood	Pellets	Wood		Pellets		
Case	1	2	3	4	5	6	7
D_x [m^2/s]	0.36 e-3	0.61 e-3	0.68 e-3	0.64 e-3	0.83 e-3	0.43 e-3	0.92 e-3
D_y [m^2/s]	0.25 e-3	0.38 e-3	0.31 e-3	0.85 e-3	0.68 e-3	0.42 e-3	0.24 e-3
D_L [m^2/s]	0.34 e-3	0.56 e-3	0.45 e-3	0.74 e-3	0.75 e-3	0.46 e-3	0.58 e-3

The lateral dispersion coefficients obtained in this work is in the same order of magnitude as reported by several of the previous investigations for bubbling or stationary beds.

Publications and Presentations:

Johanna Olsson, David Pallarès, Filip Johnsson. *Lateral solids mixing in a large-scale fluidized bed*. To be submitted for publication in 2010.

Johanna Olsson, David Pallarès, Henrik Thunman, Filip Johnsson, Bengt-Åke Andersson, Anders Victorén, Andreas Johansson.

Förbättrad förbränningsprestanda vid avfallsförbränning i FB-pannor - B addedynamikens inverkan på luft-/bränsleomblandningen, 2010, Waste Refinery Report WR01

Johanna Olsson, David Pallarès, Filip Johnsson. *Digital image analysis of bubble flow distribution – influence of operational parameters*. International Conference on Fluidization (XIII), Gyeong-ju Korea, 2010; pp 177-184.

Johanna Olsson, David Pallarès, Filip Johnsson. *Digital image analysis of bubble flow distribution – influence of operational parameters*. Poster and oral presentation, At International conference on fluidization, Fluidization XIII, Gyeong-ju Korea May 16 – 21, 2010.

Johanna Olsson, *Fluidized bed combustion – improved performance for waste fired boilers*, March 15 2010, Annual meeting of Waste Refinery

Participation in GS biofuel courses

- Thermo chemical conversion of biomass and waste (2007). Chalmers University of Technology.
- Chemistry in combustion part II (2008). Åbo Akademi

Analytical Techniques in Combustion:

- Part 1: Chalmers University of Technology, Gothenburg October 20 – 24 2008
- Part 2: Technical University of Denmark, Copenhagen February 2 – 6 2009
- Part 3: Norwegian University of Science and Technology, Trondheim May 4 – 7 2009
- Part 4: Åbo Akademi, Åbo September 21 – 25 2009

Travelling

Annual meetings (past):

- Visby, September 14 – 16 2008. Flight to Visby from Gothenburg via Sthlm. Flight to Gothenburg from Visby via Sthlm.
- Trondheim, June 14 – 16 2009. Flight to Trondheim from Gothenburg via Oslo. Flight to Gothenburg via Oslo.

Annual meetings (upcoming):

- Copenhagen, September 26 – 28 2010. Train from Gothenburg to Copenhagen. Train to Gothenburg from Copenhagen.

Chemistry in combustion, part II:

- Åbo, Nov 3-5 2008, Bus to Sthlm from Västervik, fairy to Åbo. Flight to Gothenburg from Åbo via Sthlm.
- Åbo, Nov 26-28 2008. Train to Sthlm from Gothenburg, fairy to Åbo. Flight to Sthlm from Åbo, train to Gothenburg from Västerås.

Analytical Techniques in Combustion:

- Part 2: Technical University of Denmark, Copenhagen February 2 – 6 2009. Train from Gothenburg to Copenhagen.
- Train from Copenhagen to Gothenburg.
- Part 3: Norwegian University of Science and Technology, Trondheim May 4 – 7 2009. Flight to Trondheim from Gothenburg via Oslo. Flight to Oslo, train to Gothenburg.
- Part 4: Åbo Akademi, Åbo September 21 – 25 2009. Train to Sthlm from Gothenburg, fairy to Åbo. Flight to Sthlm from Åbo, train to Gothenburg from Västerås.



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TOPIC **High temperature gas cleaning with granular bed filter**

MAIN SUBJECT **High temperature gas cleaning**

SUPERVISORS Prorektor Johan E. Hustad
Prof. Otto K. Sønju

M.Sc. **April 2007**

DOCTORAL STUDIES

Started June 2007

To be completed June 2011

High temperature gas cleaning with granular bed filter

Kavitha Pathmanathan

Background

Gas cleaning is an important issue in many technological field namely gasification, biomass combustion and waste incineration. The off-gas from gasification processes can be further utilized in gas engines, gas turbines and high temperature fuel cells to generate electricity and heat. Those utilization processes may require specific upstream gas cleaning steps including the removal of particles, tars or other pollutants to avoid damages to the downstream equipment from particle fouling and erosion effects and to allow the cleaned gas to meet the environmental emission regulations. Furthermore, harmful air emissions can pose a considerable risk to the environmental and human health. Since gas utilization occurs at high temperature, it is energetically advantageous (efficient conversion of fuel to energy) to accomplish gas cleaning those temperatures. Further, reduction of overall efficiency from blockage, clogging and corrosion due to condensation of condensable organic compounds can also be avoided with high temperature gas cleaning. However, there are a limited range of technologies available for commercial high temperature gas cleaning. The Panel Bed Filter (PBF) is one of the most promising approaches for high temperature gas cleaning.

Objectives

This paper presents experimental results from laboratory investigation of a PBF with novel louver design. The invention and patenting of the novel design (the “filter tray”) is an improvement to the earlier panel bed louver designs. The improvement aims in reducing number of gas-entry surfaces per module, number of modules per unit filter, footprint and clean-bed pressure drop. Thus, a laboratory scale PBF with the novel design was built and tested to understand the overall performance of the new design.

Method

Task 1: Laboratory investigations of new louver design, the filter tray at room temperature. The tests are conducted at various filtration parameters.

Task 2: Laboratory investigations of new louver design, the filter tray (different dimension compared to the first test rig) from room temperature to 120°C. The tests are conducted at various filtration parameters.

Task 3: Investigation with Horizontal Bed Unit (HBU) at about 200°C from a slipstream from a commercial waste power plant

Task 3: Investigation of up-scaled PBF installed at Bjertnæs Sag AS to reduce the particle emission from the exhaust gas (combustion of wood chips).

Results

- Results obtained so far illustrates that the PBF can be used for gas filtration from low to high temperature with good filtration efficiencies. Accordingly, the filter has smaller foot print compared to other types of gas filtration units and has lower clean bed pressure drop which leads to longer filtration cycles.
- Results expected in the future include the performances of the filter in full scale and also testing of a slipstream in commercial waste combustion power plant.

Publications and Presentations:

- K.Pathmanathan, O. K. Sønju, J. E. Hustad; A compact granular bed filter for high temperature synthesis gases; 4th International Conference on Clean Coal Technologies & 3rd International Freiberg Conference on IGCC & XtL Technologies, 18-21st May 2009, Dresden, Germany.
- K.Pathmanathan, O. K. Sønju, J. E. Hustad; Investigation of regeneration mode for a compact granular bed filter for high temperature filtration, International Conference & Exhibition for Filtration and Separation Technology; 13-15th October 2009, Wiesbaden, Germany.
- K.PATHMANATHAN, O. K. SØNJU, J. E. HUSTAD; A COMPACT GRANULAR BED FILTER FOR HIGH TEMPERATURE GAS CLEANING, 23RD AMERICAN FILTRATION AND SEPARATION SOCIETY (AFS) ANNUAL CONFERENCE SAN ANTONIO, TEXAS, USA, 22-25TH MARCH 2010.
- K.PATHMANATHAN, O. K. SØNJU, J. E. HUSTAD; A COMPACT GRANULAR BED FILTER FOR IGCC HOT GAS CLEAN-UP, 4TH INTERNATIONAL FREIBERG CONFERENCE, DRESDEN, GERMANY, 03-05TH MAY 2010.

Participation in GS biofuel courses

Chemistry in combustion processes part II, Åbo Akademi University, Turku, Finland, October 2007

Thermal Conversion of Solid Fuels, Chalmers University of Technology, Gotenburg, Sweden, November 2007

Analytical Techniques in combustion, Chalmers University of Technology, Gotenburg, Sweden, November, 2008

Analytical Techniques in combustion. Technical University of Denmark, Copenhagen, Denmark, February 2009

Analytical Techniques in combustion. Norwegian University of Science and Technology, Trondheim, Norway, May 2009

Analytical Techniques in combustion. Åbo Akademi University, Turku, Finland, September 2009



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Title: **Improvement in running and maintenance cost of wood-pellets based heating centrals.**

Supervisor: Prof. Johan Hustad
Cand. Agric. 1996

Doctoral studies started autumn 2006. The Ph.D. studies is done in partly time combined with a profession as a marketing manager of Bioenergy in Statoil Norge AS.

The studies is financed by Statoil Norge AS.

Background

Utilisation of bioenergy for heating purposes (not transportation) is increasing in Norway, opposite to traditional use which only has been wood industry, large district heating and heating stoves in households. Nevertheless the government goals are larger, 4 TWh growth in water based heating (mainly bioenergy) before 2010 (NOU 1998:11).

The refining degree woodpellets have achieved a certain level of utilization in Norway with a use of approximately 45 000 tons per year. This is distributed between approximately 5500 units of pellets stoves and 100 medium size heating centrals (below 3 MW). Complement to this is existent woodchips based heating centrals which also can use woodpellets. Woodpellets are seen as a necessary degree of refined biomass to reach conversion goals from small- and medium size users of oil and electricity in the stationary sector/heating purposes.

The benefits of wood-pellets, which are important when use in new areas are to be made, are as follows:

- a relatively homogenius fuel
- an easy fuel to trade
- quality standards is established
- very high energy content regarded to volume

- Transportation and handling is done in closed systems with pressure air.
- Wood-pellets is dry, and problems with fungus, air quality in storage-rooms and freezed material is non-existing.
- An easy fuel should increase the possibilities to increase both environmental and economic prestations regarding all conversion technologies.

Woodpellets and biomass in general compete mostly against electricity and to some extent heating oil.

Therefore end-user comfort and perspectives is important to increase use in Norway. Since Norway is a country with a large lack of water-based heating systems, maintenance personell is not used to both boilers and these heating systems. In addition, many installations is using wood-pellets, but the boilers is designed for wet wood-chips with a weak running prestations as a result.

In a holistic view, introduction is not only a technical challenge but also include the operators capability and willingness to use bioenergy.

Objectives

- Investigate the system fuel-heating central- personel introduction and point out potentials for improvement
- What properties should wood-pellets heating plants have to credit a standardized fuel as wood-pellets with higher reliability and lower running costs?
- Investigate and make developments to increase low output and on/off running conditions
- Due to lack of traditional raw materials for pellets productions, investigate new interesting ones like pine pulpwood with bark and lignin residues from 2G-ethanol production

Method

- Task 1. Through the discipline systems engineering and a questionnaire investigate the system fuel-heating central-personel and point out potentials for improvement in the whole system.
- Task 2. Production of wood-pellets from pine pulpwood with bark; fresh and 6 month aged. Fuel quality and combustion behaviour
- Task 3. Production of wood-pellets from pine pulpwood with added pure lignin. Fuel quality and combustion behaviour.

Publications and presentations

Norwegian households' perception of wood pellet stove compared to air-to-air heat pump and electric heating Original Research Article *Energy Policy*, Volume 38, Issue 7, July 2010, Pages 3744-3754
Bertha Maya Sopha, Christian A. Klöckner, Geir Skjevrak, Edgar G. Hertwich.

Changes in the chemical composition of wood material during pellets production and storage and drying of the raw material. Geir Skjevrak, Janka Dibdiakova, Riada Jirjis, Olav Høibø. Article in progress.

The influence of storage and drying methods for Scots pine raw material on mechanical pellet properties and production parameters. Tore Filbakk, Geir Skjevrak, Janka Dibdiakova, Riada Jirjis, Olav Høibø. Article sent to Fuel Processing Technology june 2010.

2 G Hydrolysis residue; properties of pelletized fuel in mixture with stemwood of Pine. Geir Skjevrak, Liang Wang. Article in progress.

Mixture of sintering reducing additives in pellets; mechanical fuel properties and combustion tests. Geir Skjevrak. Liang Wang. Article in progress.

Results

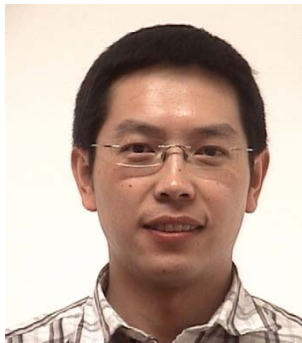
Plan to finish Ph.D during 2011.

Participation in GS biofuel courses

No participation in GS biofuel courses. Tried to participate on combustion course in Dk august 2010, but the course where cancelled.

Travelling

No travelling



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TOPIC **Biomass combustion, ash chemistry,
additives**

MAIN SUBJECT **Biomass combustion, ash chemistry,
additives, deposits**

SUPERVISORS Main supervisor: Professor Johan E. Hustad
Co-supervisor: Dr Morten Grønli

M.Sc. **Mechanical Engineering, Thermal Energy**

DOCTORAL STUDIES

Started September, 2006

To be completed Spring, 2011

Effect of additives in reducing slagging and deposition in biomass combustion applications

Liang Wang

Background

Biomass can make a substantial contribution to supply future energy demand in a sustainable way. Among different utilization methods, combustion is the most widely applied technology to convert the biomass into power, electricity and heat. However, due to the high ash and problematic inorganic elements content in biomass, many of operation problems are encountering with combustion of biomass materials. The key technical ash related problems during biomass combustors and boilers are fouling deposits, high temperature corrosion, formation of fused or partly fused agglomeration and slagging deposits, and aerosol emissions. It has been proved that additives with different active compositions could reduce or eliminate the ash related problems by means of chemical/physical adsorption, chemical reactions and dilution effects. Different additives have been investigated in previous work with promising results, especially for the aluminium-silicon system based additives such as kaolin. However, the commercial additive like kaolin is not financial attractive due to the high costs for industry. More cheap and relative effective additives are needed with potential to be utilized in a industry scale and with large amount available. It is an interesting option to obtain more additives candidates from different waste materials with benefit to disposal waste at the same time. In this work, different additive candidates have been selected and investigated by means combustion with problematic fuels regarding to reduce ash sintering, slag formation and deposits formation.

Objectives

Due to high cost and small amount availability of commercial additives such as kaolin, more additive candidates with ability to reduce ash related problems should be found and investigated. To obtain cheap and relative high efficient additives from waste materials is an interesting option. In this work, the additives from waste materials were investigated in terms of ability to reduce biomass ash melting and sintering, slag formation in residential combustion appliances and deposits formation in an entrained flow reactor. The biomass ash fusion behaviour, slag and deposits formation tendency were evaluated when biomass combusted with and without addition of studied additives. Different analytical techniques were applied to investigate the influence from additive to biomass ash chemistry.

Method

1 Fuel and additives selection and characterization. Two kinds of biomass fuel (Danish wheat straw and waste wood) were selected due to high problematic properties during combustion. Three additive candidates from waste materials (sewage sludge, marble sludge, clay sludge) were selected based on potential positive effect on biomass combustion. Both

fuels and additives were characterized regarding to proximate, ultimate, ash compositions, heating value, fuel behaviour and thermal properties.

2 Evaluation influences of additives candidates on biomass ash melting and sintering behaviour. With laboratory ashing procedure, the ashes from biomass combustion with and without additives addition were produced. Fusion and sintering test were performed on all ash samples with further XRD and SEM-EDX analysis.

3 Combustion tests of waste wood with and without sewage sludge and marble sludge addition in an industry scale boiler. Slagging tendency of waste wood combustion with and without additives were evaluated by collecting and sorting ash residues after combustion based on sintering degree and particle size distribution. The collected samples were further characterized with XRF, XRD and SEM-EDX analysis for obtaining detailed chemical composition, mineralogical and chemistry information.

4 To investigate the effects of sewage sludge addition on wheat straw and waste wood combustion, experiments have been carried out with burning of these two fuels in an entrained flow reactor that simulates conditions in pulverised combustion furnace with high temperature and short reaction time. The deposits, fly ash, aerosol and bottom ashes were collected after each test. During the test, the SO_x and NO_x emission were logged as indication of combustion efficiency. All collected ash residues were characterized for chemical compositions including bulk chemical compositions and water soluble element content. In addition, the ash residues were analyzed with XRD and SEM-EDX analysis to get more information about ash transformation and chemistry information.

Results

1 Fuel and additives characterization. Both Danish wheat straw and waste wood contain high content of alkali metal and chlorine that cause operation problems during combustion. Extra interests were put on the sewage sludge, since the investigation about the sewage sludge combustion and ash properties are quite limited. In this work, three kinds of sewage sludge were obtained from different wastewater processing plants with utilization two precipitation agents (Al₂SO₄ and Fe₂SO₄) for phosphorus recovery. The sintering behavior and mineral transformation of the ashes from three sewage sludge were characterized by means of ash production, chemical composition analysis, fusion temperature measurement, mineral phases identification (XRD) and SEM-EDX analysis. It was found that the utilization of phosphorus precipitation chemicals has a significant influence on sewage sludge ash properties. The elements (Al and Fe) were enriched due to application of two agents. As a consequence, the Al rich sewage sludge ash high melting temperature and low sintering tendency compared with Fe rich sewage sludge. Fe rich sewage sludge ash is more active during heating process with observation of radical melting and mineral appearance and disappearance observed by

XRD. Combined with XRD and SEM-EDX analysis, the sintering mechanisms of Fe rich sewage sludge ash were proposed.

2 The performance of three additives for reducing biomass ash sintering was evaluated based on lab scale experiments. It was found that sewage sludge (Al rich) is the most effective additive to increase biomass ash melting temperature. The XRD analysis results reveal that more Al_2O_3 was introduced into ash residues, which are high temperature inert to lower the biomass ash sintering tendency. In addition, formed new mineral phases could also explain the increased biomass melting temperatures. Marble sludge is not reactive as observed by XRD and SEM-EDX analysis, since calcium is the main composition of marble sludge. However, the sintering behavior of biomass ash decreased with addition marble sludge, which is mainly caused by dilution effect. The interesting results are that addition of clay sludge decreased the waste wood ash fusion temperature in specified addition amount. The possible reason is that added silicon from clay sludge is favored for formation of alkali silicates, since the alkali content in waste wood is relative high. Moreover, some clay minerals are active under high temperature and may lead the melting of ash.

3 Based on the lab scale tests, sewage sludge and marble sludge were tested as additives when waste wood combusted in an industry scale boiler (1.2 MW). Waste wood in study showed high slagging tendency with 32% inlet fuel ash formed into hard slag. XRD and SEM-EDX results suggest that formation of low melting temperature potassium aluminum silicate is the main reason for high slagging tendency. With addition of sewage sludge, the slag sintering degree decreased with formation more slag with small particle size. However, with high sewage sludge addition ratio, the slagging tendency of waste wood increased dramatically due to high inlet ash amount and potential negative effect from degraded sands/soil from sewage sludge. The slagging tendency of waste wood was eliminated with addition of marble sludge, with only 10% inlet fuel ash was sintered into slag. SEM-EDX analysis results reveal that calcium from marble sludge may prevent attach and accumulation of melted waste wood ash.

4 The results from combustion of Danish wheat straw and waste wood fuel with and without addition of sewage sludge showed that addition sewage sludge reduced the deposits on sampling probe with low addition ration. As the sewage sludge addition amount increased to 10% of inlet fuel in weight percentage, the deposits rate increased. XRD analysis for the collected ash residues showed that sewage sludge addition changed the deposits mineral phases from alkali rich chlorides and silicates to alkali aluminum silicates, aluminum oxides and phosphorus/calcium rich phases. The water soluble elements in both deposits and cyclone ash decreased when wheat straw burned with addition of sewage sludge. SEM-EDX results reveal that the KCl amount in wheat straw combustion deposits

decreased with replacement of more aluminum rich fine particles that were introduced from sewage sludge.

Almost of all experimental work and analysis are finished now. But due to the operation problems and maintenance of some instruments (SEM-EDX and XRD), some of work are heavily delayed. Fortunately, it is manageable to start the analysis in other labs. It is one of the main reasons for the delay of PhD study progress. Now, main work is papers and thesis writing.

Publications and Presentations:

Publications:

L. Wang, J. Hustad. Alkali chlorides related fouling and corrosion in biomass combustion, 1st NTVA-CAE Joint Seminar on Strategy, Research and Development in Renewable Energy, pp. 225-239. Beijing, China.

Liang. Wang., Johan E. Hustad., Morten Grønli. Influence of Additives on Biomass Ash Characteristics. Proceeding of 17th European Biomass Conference and Exhibition, P1206-1211. Hamburg, Germany. June 29th-03th, 2009

Liang. Wang., Johan E. Hustad., Morten Grønli. Sintering Behaviour of Wheat Straw Ash with Addition of Additive under Elevated Temperature. Proceeding of 18th European Biomass Conference and Exhibition, P1206-1211. Lyon, France, May 3th-7th. 2010. ISBN:978-88-98407-56-5.

Liang. Wang., Geir Skjevraak., Johan E. Hustad., Christer Heen Skogland. Effect of Additives in reducing slagging and corrosion in biomass combustion applications. Proceeding of The Renewable Energy Research Conference 2010. (2010).Trondheim, Norway

Liang. Wang., Johan E. Hustad., Morten Grønli. Sintering and Mineral Transformation of Sewage Sludge Ashes. August 29th-September 3th, 2010.Lapland, Finland

Oral presentations:

1 Liang Wang., Johan E. Hustad. Alkali chlorides related fouling and corrosion in biomass combustion, 1st NTVA-CAE Joint Seminar on Strategy, Research and Development in Renewable Energy, (2008), Beijing, China

2 Liang. Wang., Johan E. Hustad., Morten Grønli. Influence of Additives on Biomass Ash Characteristics. 17th European Biomass Conference and Exhibition. (2009).Hamburg, Germany.

3 Liang Wang., Geir Skjevraak., Johan E. Hustad. Effect of Additives in reducing slagging and corrosion in biomass combustion applications. The Renewable Energy Research Conference 2010. (2010).Trondheim, Norway

4 Liang Wang, Johan E. Hustad, Moten Grønli. Sintering Characteristics and Mineral Transformation of Sewage Sludge Ashes. IMPACTS OF FUEL QUALITY, (2010), Lapland, Finland.

Participation in GS biofuel courses

Chemistry in combustion processes part II, Åbo Akademi University, Turku, Finland. 22th-26th, October, 2007

Analytical Techniques in combustion. Technical University of Denmark, Copenhagen, Denmark. 2th-6th. February, 2009

Analytical Techniques in combustion. Norwegian University of Science and Technology. 4th-7th. May. Trondheim, Norway.

Conference

17th European Biomass Conference and Exhibition, 29 June-03 July, 2009, Hamburg, Germany

18th European Biomass Conference and Exhibition, P1206-1211. Lyon, France, May 3th-7th.

Impacts of Fuel Quality on Power Production and Environment, (2010), Lapland, Finland.

Seminar

Nordic Graduate School of Biofuel Science and Technology, Annual seminar 2007, 26th-28th, September, Turku, Finland

Nordic Graduate School of Biofuel Science and Technology, Annual seminar 2008, 14th-16th, September, Visby, Sweden

Nordic Graduate School of Biofuel Science and Technology, Annual seminar 2009, 14th-16th, June, Trondheim, Norway

Experiment cooperation

1 Experiment work in CHEC in DTU from 24th, May to 14th June, 2009.

2 Experiment work in CHEC in DTU from 1th, July to 14th July, 2009.

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TOPIC **CFD-based modeling of black liquor char beds**

MAIN SUBJECT **Inorganic Chemistry**
SUPERVISORS **Prof. Mikko Hupa**
Doc. Christian Mueller
Dr. Anders Brink

M.Sc. **June 2005**

DOCTORAL STUDIES

Started **January 2006**

Completed **June 2010**

Modeling and field observations of char bed processes in black liquor recovery boilers

Markus Engblom

Background

With the development of more sophisticated models, computational fluid dynamics (CFD) is today considered a valuable research and engineering tool for studying industrial scale combustion processes.

The increase in the unit size of black liquor recovery boilers is largely contributed to better understanding of the furnace processes. CFD has had a central role in this development.

The black liquor recovery boiler is similar to other types of steam boilers in various respects, e.g. water walls and superheaters are installed for steam production, and combustion air is introduced at multiple levels. However, in the black liquor recovery boiler, the fuel and combustion air are introduced entirely separately. Figure 1 presents a schematic picture of the lower furnace of a recovery boiler.

Black liquor is introduced into the recovery furnace as a relatively coarse spray. Droplet diameters ranging from less than 1 mm to 10 mm or more have been reported. Droplet size is affected by the geometry of the liquor gun and the operating conditions. The black liquor droplets undergo in-flight combustion and, ideally, reach the furnace bottom while burning to form the char bed. In the char bed, the organic matter continues to burn and the inorganic matter separate from the char and flow out of the furnace into the smelt dissolving tank.

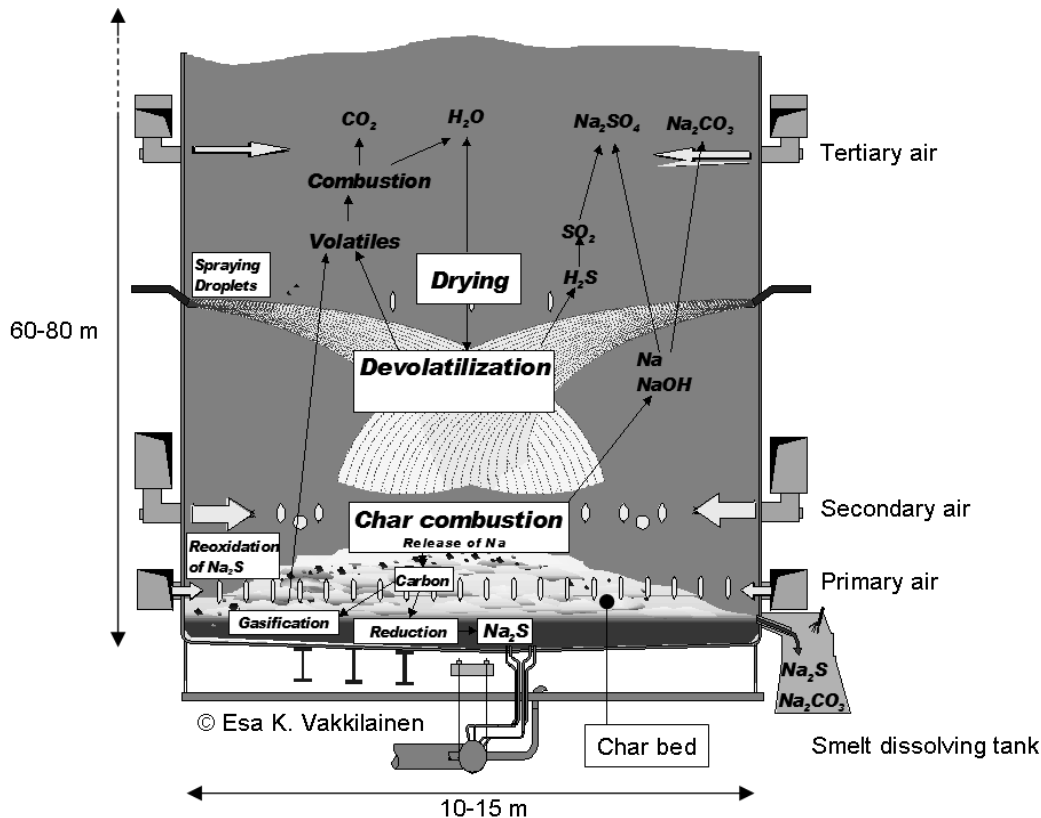


Figure 1. Schematic picture of lower furnace processes. Characteristic furnace dimensions of modern black liquor recovery boilers are also indicated.

Black liquor combustion modeling requires sub-models for droplet conversion, gas phase combustion and char bed combustion. Although char bed models have become more detailed and refined, the shape of the char bed has been presumed in these models. The presumed bed shape has been sufficient for overall numerical studies of black liquor combustion, but for more detailed studies of the char bed processes, the bed shape should be determined by the combustion process. Description of relevant physical and chemical bed processes is a requirement for a model to predict correctly the behavior of a char bed, including burning rates and shape.

Objectives

- To continue development of a char bed model by including a feature that describes change in bed shape
- Identification and inclusion of physical and chemical char bed processes relevant for bed shape
- Model validation by comparison with observations from real furnaces
- Use of model to gain insight into char bed processes

Method

- Use of commercial CFD software
- Development of sub-models
- Comparison of simulation results against observations from real furnaces

Results

Char bed shape model

The starting point for the char bed shape model was a char bed burning model which utilized a fixed bed shape¹. The model calculates the carbon accumulation rate on the bed surface as the difference between the char carbon in black liquor droplets reaching the char bed and the char carbon converted on the bed. Figure 2 shows predicted carbon accumulation, positive accumulation indicating local bed growth and negative accumulation indicating local bed depletion.

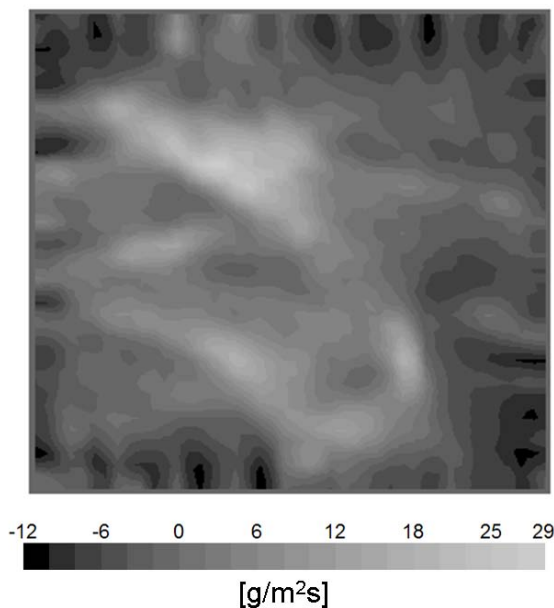


Figure 2. Carbon accumulation predicted by char bed burning model¹.

The char bed burning model was extended to include a feature for describing change in bed shape². In the bed shape model a change in bed shape is made based on the predicted carbon accumulation. The model calculates the new positions of the calculation grid nodes on the bed surface. Calculation of the bed shape is carried out as a sequence of time steps. The magnitude of the time step is chosen such that a relatively small change in bed shape occurs during one time step.

Recovery boiler simulations

Simulations were carried out for two existing recovery boilers; the boilers A and B. In Boiler-A simulations the extended char bed model was tested for its response to changes in droplet size in the black liquor spray. Figure

¹ Bergroth, N., Engblom, M., Mueller, C., Hupa, M., *CFD-based modeling of kraft char beds – part 1: char bed burning model*, Tappi J. 9(2), 6-13, 2010.

² Engblom, M., Mueller, C., Brink, A., Hupa, M., Jones, A. *Toward predicting the char bed shape in kraft recovery boilers*, Tappi J. 7(10), 12-16, 2008.

3 presents predicted bed shapes. With an average droplet diameter of 2 mm the char bed was depleted. With average droplet diameters 3.1 mm and 6.3 mm the char bed grew. The response of the model agrees with experience from real recovery boilers, where droplet size is used for controlling char bed size. With smaller droplets a greater share of char burning takes place in-flight, whereas with larger droplets more char carbon is delivered to the char bed.

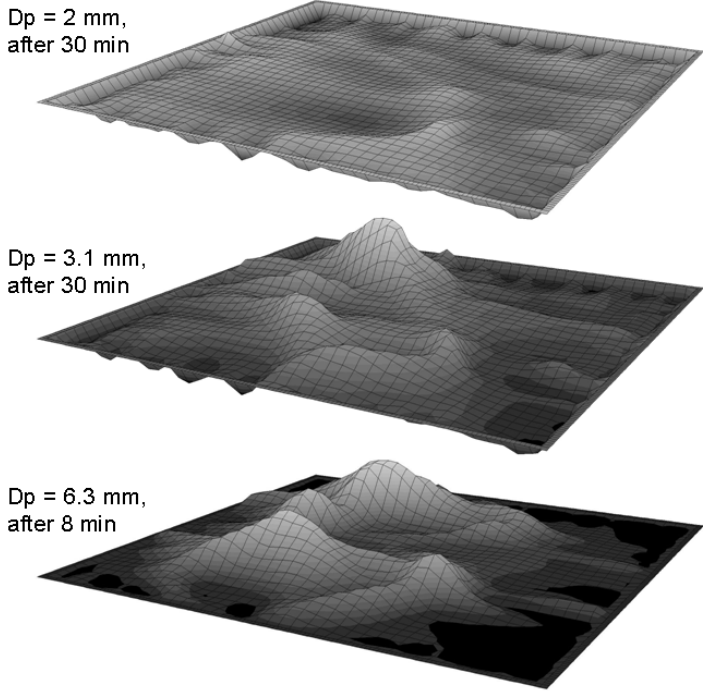


Figure 3. Predicted bed shapes when starting from a flat bed shape and using three different average droplet sizes in the black liquor spray². The predicted bed shapes were compared with the shape of the real char bed in Boiler A. The simulated bed shape when using average droplet size 3.1 mm agreed well with the shape of the real char bed; Figure 4 present the comparison.

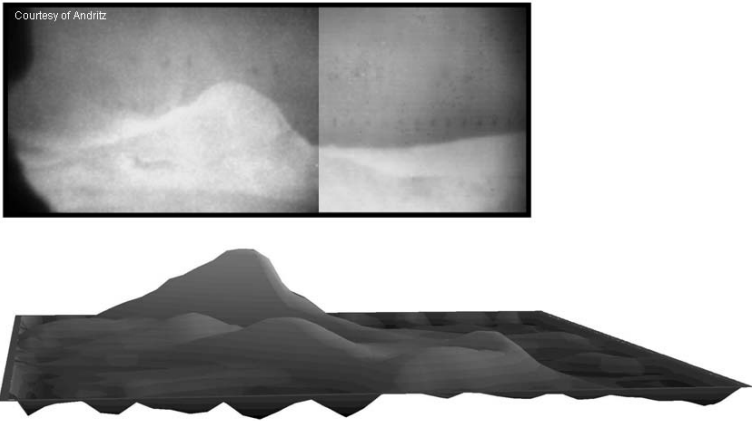


Figure 4. Real (upper) and simulated bed shape (lower) when using average droplet size 3.1 mm².

As basis for Boiler-B simulations, the real recovery boiler char bed was operated in three different modes: stable, growing, and depleting³. Liquor spraying was the main operational parameter which was altered to change from one operational mode to the other.

Simulations of recovery boiler B were set up with good knowledge of the operational parameters. Effort was also invested in obtaining representative boundary conditions for the liquor spray, including direction and droplet size distribution. Three simulation cases were calculated, corresponding to the three char bed operational modes.

Of the three simulation cases, Case 1 corresponds to the situation of stable char bed operation. The char bed burning model predicted carbon depletion. However, since the initial bed shape used in Case 1 was flat, with a vertical position equal to the level of smelt no changes in bed shape were simulated.

In Case 2 simulation the char bed was predicted to grow (Figure 5), and in Case 3 simulation the char bed was predicted to deplete (Figure 6). The growth and depletion in cases 2 and 3, respectively, agree with the behavior of the real char bed during the corresponding operational modes.

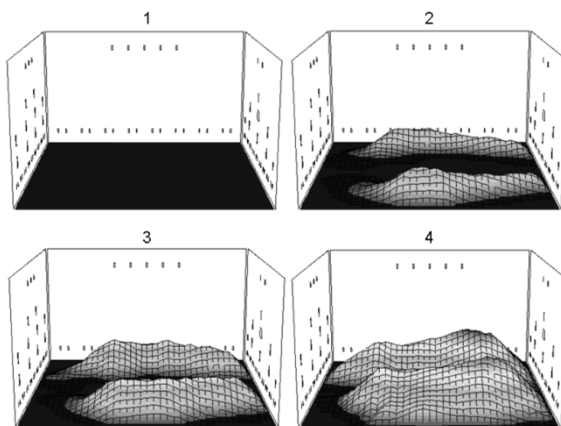


Figure 5. Development of predicted bed shape in Case 2 simulation, corresponding to the operation of the real char bed in a growing mode³.

³ Engblom, M., Rönqvist, A., Brink, A., Mueller, C., Jones, A., Hupa, M., *Recovery Boiler Char Bed Dynamics – Measurements and Modeling*, International Chemical Recovery Conference Proceedings, Vol.1, pp.119-133, Tappi Press, 2010.

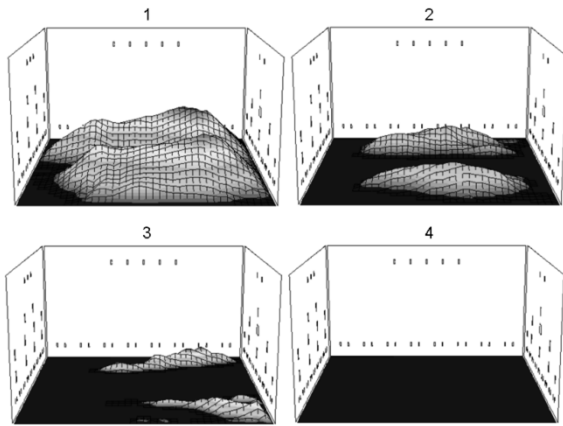


Figure 6. Development of predicted bed shape in Case 3 simulation, corresponding to the operation of the real char bed in a depleting mode³.

Conclusions

- An existing char bed model was extended to include a char bed shape predicting feature.
- Results from simulation of two existing recovery boilers confirmed the current quantitative understanding of char bed burning.

Publications and Presentations:

Li, B., Brink, A., Engblom, M., Mueller, C., Hupa, M., Kankkunen, A., Miikkulainen, P., Fogelholm, C-J., *Spray models for CFD of black liquor recovery furnaces*, 15th IFRF Members Conference, Pisa, Italy, 2007.

Engblom, M., Brink, A., *Influence of Stefan flow and boundary layer reactions on surface reaction rate*, Nordic Section of the Combustion Institute - Biennial Meeting, Åbo, 2007.

Brink, A., Engblom, M., Hupa, M., *Nitrogen oxide emission formation in a black liquor boiler*, Tappi J. 7(11), 28-32, 2008.

Engblom, M., Mueller, C., Brink, A., Hupa, M., Jones, A. *Toward predicting the char bed shape in kraft recovery boilers*, Tappi J. 7(10), 12-16, 2008.

Engblom, M., Brink, A., Mueller, C., Hupa, M., *CFD-based modeling of laboratory scale kraft char bed burning*, 8th European Conference on Industrial Furnaces and Boilers (INFUB-8), Portugal, 25-28 March 2008.

Engblom, M., Brink, A., Mueller, C., Hupa, M., *CFD modellering av sodapannor vid Åbo Akademi*, Sodahuskonferens, Stockholm, 13 November 2008.

Hupa, M., Engblom, M., Brink, A., Mueller, C., *How well do we understand recovery furnace processes?*, Finnish Recovery Boiler Committee 45th Anniversary International Recovery Boiler Conference, Lahti, Finland, June 3-5, 2009.

Bergroth, N., Engblom, M., Mueller, C., Hupa, M., *CFD-based modeling of kraft char beds – part 1: char bed burning model*, Tappi J. 9(2), 6-13, 2010.

Engblom, M., Bergroth, N., Mueller, C., Jones, A., Brink, A., Hupa, M., *CFD-based modeling of kraft char beds – part 2: a study on the effects of droplet size and bed shape on bed processes*, Tappi J. 9(2), 15-20, 2010.

Engblom, M., Rönqvist, A., Brink, A., Mueller, C., Jones, A., Hupa, M., *Recovery Boiler Char Bed Dynamics – Measurements and Modeling*, International Chemical Recovery Conference Proceedings, Vol.1, pp.119-133, Tappi Press, 2010.

Engblom, M., Brink, A., Mueller, C., Hupa, M., Jones, A., *Reactive Boundary Layers in Kraft Char Bed Burning – Part 1: Mathematical Model*, submitted for publication.

Engblom, M., Brink, A., Mueller, C., Hupa, M., Jones, A., *Reactive Boundary Layers in Kraft Char Bed Burning – Part 2: Model Predictions Vs. Experimental Results*, submitted for publication.

Engblom, M., *Modeling and field observations of char bed processes in black liquor recovery boilers*, PhD thesis, Åbo Akademi University, Process Chemistry Centre, Laboratory of Inorganic Chemistry, Report 10-01, 2010.

International co-operation in addition to BiofuelsGS-2

External PhD thesis supervisor: Andrew Jones, International Paper Inc.

Travelling

- BiofuelsGS-2 Annual Seminar, Kimito, Finland 26-28.9.2007.
- 8th European Conference on Industrial Furnaces and Boilers (INFUB-8), Portugal, 25-28 March 2008.
- Sodahuskonferens, Stockholm, 13 November 2008.
- BiofuelsGS-2 Annual Seminar, Visby, Sweden 14-16.9.2008.
- BiofuelsGS-2 Annual Seminar, Inderøy, Norway 14-16.6.2009.
- Finnish Recovery Boiler Committee 45th Anniversary International Recovery Boiler Conference, Lahti, Finland, June 3-5, 2009.

- International Chemical Recovery Conference, Williamsburg, Virginia USA, 29 March – 1 April, 2010.
- BiofuelsGS-2 Annual Seminar, Kopenhagen, Denmark 26-28.9.2010.



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TOPIC **Waste combustion**

MAIN SUBJECT **Inorganic reactions in waste combustion**

SUPERVISORS Docent Bengt-Johan Skrifvars,
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PhD Andreas Johansson
Professor Mikko Hupa

M.Sc. **June 2007**

DOCTORAL STUDIES

Started September 2007

To be completed August 2012

Chemical methods to study waste fuels

Frida Claesson Jones

Background

This 3 year work is a study of the chemical content and variation within waste fuels from two full-scale plants in Sweden, Plant A and B. Conventional fuel analyses were performed, followed by a study where the chemical information from the analyses was used as input data for thermodynamic equilibrium calculations to predict the formation of alkali and metal compounds during combustion. As a complement to the conventional fuel analysis two different fractionation methods were used, with the main focus being on comparing the methods. Within this work two conference articles have been written. The first article is focused on thermodynamic equilibrium calculations with the fuel mix from Plant B. The second article includes variation data from both plants and an additional study of dioxin content in the fuel.

Initially, there was a 12-month fuel sampling period from September 2007 to October 2008, providing representative samples by using two different techniques owing to different preparation methods in the two plants. The ultimate analyses (C, H, N) showed that the waste fuel composition was similar throughout the sampling period both for the fuel mixture from the grate-fired boiler (Plant A) and the fuel mixture from the BFB boiler (Plant B). As expected the variation of ash-forming elements, for example, Na, K, and Zn, was larger, and the differences between the two different plants was also more significant for these elements. Furthermore, trace metals were present in low concentrations and showed the widest relative variation for both plants. The fuel mixture from Plant A had a somewhat larger spread around the average value of the ash forming material, which is related to the more heterogeneous fuel mixture. It can be concluded from this work that repeatable fuel samples are necessary to obtain a good overview of the fuel composition. Single samples can divert significantly from an average of samples collected during a longer period. This conclusion is further supported by the analyses of the October 2007 sample from Plant A that was divided into two bags and analysed as two separate samples. The results are similar but differ for some elements, showing the importance of taking more than one sample.

The result achieved in this work provides knowledge about the inorganic content of waste. Trends and variations in the fuel composition over a 12-month period rather than one single sample enhance the possibility of predicting fuel-related combustion problems such as slagging, fouling, and corrosion. Improvements in the knowledge about waste fuels facilitate pre-active selection of waste fractions to be burned, and result in higher boiler availability, increased power production, and less maintenance cost. Furthermore, the work shows that two separate chemical fractionation methods could be combined to make the procedure more economical, more beneficial, and less time-consuming.

Future work

The next step in the research is to study deposit formation from waste combustion in a controlled lab-scale environment. By comparing reference cases to experiments with addition of inert particles, ash from sewage sludge, sulfur and/or chlorine, a more detailed knowledge about deposit formation in waste combustion is gained. The fuel used in the study will be sampled from a full-scale plant and chemically analyzed and pelletized before combustion. The combustion test will be performed in a 15 kW fluidized bed and deposits will be collected on deposit probes.

Objectives for future work

1. Increased understanding of the effects of increased accessible reaction surface on deposit formation.
2. Increased understanding of how S affects the alkali reactions, with and without additional inert particles in the fuel.
3. Increased understanding of how the bed temperature affects deposit formation.
4. Increased understanding of how the combustion environment (reducing/oxidizing) affect deposit formation.

Method

1. Taking fuel samples from full-scale plants by using the method from the first part of the doctoral studies.
2. Lab-scale tests with added material like inert particles and sewage sludge. Changes of parameters like bed temperature, available oxygen, addition of Cl and/or S etc.

Travelling Sept 2007- Sept 2010

The phd-work has been carried out at University of Borås and SP Technical Research Institute of Sweden with supervision and guidance from Åbo Akademi. During the phd-studies some courses have required travelling. A list of courses and locations is presented below. Travelling within BioFuelGS-2 has been financed by the Nordic school. Travelling to other courses outside Sweden has been financed by the University of Borås. Travelling to conferences, one in Finland, one in China, and one in Italy (see conference list below) have been financed by the University of Borås.

Course	Study points	Location	Dates/period
Thermal conversion of solid biomass and waste (CTH, BioFuelGS)	5 sp	Sweden	19-23/11 2007
Informationssökning och informationshantering (CTH)	3 sp	Sweden	12, 14 & 18/12 2007
Energy from waste combustion and recovered materials (TKK)	3 sp	Finland	30-31/1 & 1/2 2008
FPK1 (ÅA)	4 sp	Finland	10-14/3 2008
FPK2 (ÅA)	5 sp	Finland	3-5 & 26-28/11 2008
Analytical Techniques in Combustion (BioFuel-GS2, CTH, DTU, NTNU, ÅA)	10 sp	Sweden, Denmark, Norway, Finland	20-24/11 2008, 2-6/2 2009, 4-7/5 2009, 21-25/9 2009
Organic Aerosols (GU)	3 sp	Sweden	22-25/6 2008
Emission, spridning, omvandling och deponering av föroreningar (GU)	7 sp	Sweden	26/3-28/4 2009
English for research writing (HiK)	8 sp	Sweden	26/8-27/11 2009
Miljöekonomi (ÅA)	5 + 5 sp	Sweden/ Finland	7/10 2009 –18/2 2010
Essay based on: "The development of chemical principles" Cooper H Langford och Ralph A Beebe	1 sp	Sweden/ Finland	March-April 2010
Essay based on: "Fundamentals of air pollution engineering" Richard C. Flagan och John H. Seinfeld	1 sp	Sweden/ Finland	March-April 2010

Conference	Dates
4 th Biennial Meeting of the Scandinavian-Nordic Section of the Combustion Institute, Åbo/Turku, Finland	5-6/11 2007
20 th International Conference on Fluidized Bed Combustion, Xi'an, China	18-20/5 2009
12 th International Waste Management and Landfill Symposium, Sardinia, Italy	5-9/10 2009

Publications and Presentations:

Some of the publications are not directly related to the PhD-work, but have been produced parallel to it. Some publications are only available in Swedish.

Scientific journals

Bäfver; L. S., Rönnbäck, M., Leckner, B., Claesson, F., Tullin, C., "Particle emission from combustion of oat grain and its potential reduction by addition of limestone or kaolin", Fuel Processing Technology 90 (2009) 353–359

Proceedings for Conferences

Claesson, F., Wikström Blomqvist, E., Johansson, A., Skrifvars, B-J., Andersson, B-Å., "Annual Variation In Elemental, Dioxin And PCB Content Within Swedish Waste Fuels – Results From Two Plants", Published in the proceedings and presented at the 12th International Waste Management and Landfill Symposium, October 5-9, 2009, Sardinia, Italy

Rönnbäck, M., Johansson, M., Claesson, F., "Combustion tests of pellets from ash rich biomasses in residential pellet burners", Proceedings of the International Conference on Solid Biofuels, August 12-14, 2009, Beijing, China

Claesson, F., Skrifvars' B-J., Elled, A-L., Johansson, A., "Chemical characterization of waste fuel for Fluidized bed combustion", Published in the proceedings and presented at the 20th International Conference on Fluidized Bed Combustion, May 18-20, 2009, Xi'an, China

Claesson, F., Johansson, L., Rönnbäck, M., Johansson, M., Tullin, C., "Particle emissions from combustion of oat grain with additives", Published in the proceedings and presented at the 4th Biennial Meeting of the Scandinavian-Nordic Section of the Combustion Institute, November 5-6 2007, Åbo/Turku, Finland

Rönnbäck, M., Arkelöv, O., Johansson, M., Johansson, L., Tullin, C., Claesson, F., "Methods to reduce sulphur dioxide, hydrogen chloride and particle emissions from small-scale combustion of energy grain", Proceedings from the 15th European Biomass Conference & Exhibition, May 7-11, 2007, Berlin, Germany

Reports

Andersson, S., Blomqvist, E., Bäfver, L., Claesson, F., Davidsson, K., Froitzheim, J., Karlsson, M., Pettersson, J., Steenari, B-M., "Minskad pannkorrosion med svavelrecirkulation", Waste Refinery-rapport, WR-07, 2010, SWE

Niklasson, F., Pettersson, A., Claesson, F., Johansson, A., Gunnarsson, A., Gyllenhammar, M., Victorén, A., Gustafsson, G., "Sänkt bäddtemperatur i fluidpannor för avfallsförbränning – etapp 2" Waste Refinery-rapport, WR-19, 2010, SWE

Niklasson, F., Haraldsson, C., Claesson, F., "Online-mätning av oorganiska komponenter i rökgas", Waste Refinery-rapport, WR-29, 2010, SWE

Pettersson, A., Claesson, F., "Kemisk fraktionering av avfallsbränslen – en jämförelse av metoder" Waste Refinery-rapport, WR-18, 2009, SWE

Niklasson, F., Haraldsson, C., Claesson, F., Bäfver, L., Ryde, D., "Sänkt bäddtemperatur vid termokemisk omvandling av svåra bränslen", Värmeforskrappport A08-812, 2009, SWE

Claesson, F., Blomqvist, E., Optimerad avfallshantering i Viareds Företagsförening, Energiteknik, SP Rapport 2009:06, SWE

Rönnbäck, M., Johansson, L., Claesson, F., "ERA-Net Evaluation of technology status for small-scale combustion of pellets from new ash rich biomasses- combustion tests in residential burners", Energiteknik, SP Rapport 2008:31, SWE

Rönnbäck, M., Johansson, L., Claesson, F., Johansson, M., "Karaktärisering och reduktion av stoft vid eldning av spannmål", Energiteknik, SP Rapport 2008:04, SWE



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TOPIC **Modeling biomass combustion**

MAIN SUBJECT **Inorganic Chemistry**

SUPERVISORS

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M.Sc.

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DOCTORAL STUDIES

Started

June 2008

To be completed

May 2012

Characterizing biomass fuel samples for particle combustion modeling

Oskar Karlström

Background

Globally solid fuel combustion continues to be important. Most of the solid fuel combustion concerns combustion of coals, but combustion of solid biomass is becoming more and more important. In order to improve efficiency and minimize emissions of large-scale combustion boilers, the modeling technique CFD plays an important role. One of the main critical points in CFD-modeling of solid fuel combustion is the use of simplified single particle sub-models for drying, devolatilization and char combustion. Such models require various types of fuel specific parameters: kinetic parameters, reaction order parameters, fragmentation parameters, shrinkage parameters, ash inhibition parameters, porosity parameters etc. that are determined from experiments or estimated with other methods. In many cases there is, however, no consensus on which types of single particle models that should be used as sub-models in CFD-codes. As a consequence there is no consensus on which fuel specific parameters that should be determined, since fuel specific parameters generally are also model specific.

Objectives

Develop simple and fast methods that find necessary information for modeling the thermal conversion of biomass particles in models that can be included as sub-models into CFD-codes.

Method

- A single particle furnace has been used for characterizing large biomass particles (>2mm) for single particle modeling. C-, N- and S-releases have been measured for spherical wood particles, straw-, wood- and olive pellets during devolatilization and char combustion/gasification at realistic temperatures. Moreover the shrinkages have been measured throughout the conversion. The idea is to fit modeled C-, N-, and S profiles to experimental measurements in order to determine fuel specific parameters.
- Combustion history data from a drop tube reactor has been used in order to characterize pulverized fuel particles (<1mm) for single particle modeling. The combustion data is unpublished and available in the IFRF solid fuel data base. Drop tube experiments have been performed on more than 130 different fuels. The idea is to fit modeled burnout profiles to experimental burnout profiles in order to determine fuel specific parameters for CFD-modeling. New parameter optimization methods are applied and further developed.

Results

Modeled drying, devolatilization and char combustion rates of spherical wood particles have successfully been compared to experimentally measured rates at reactor temperatures between 800 and 1100 °C and 3 % O₂ (see Fig. 1 and Fig. 2). An optimization method for determining devolatilization parameters, for a CFD-applicable model, has been developed. The method will be used for determining parameters describing S-, N- and C-release during the devolatilization of biomass pellets at combustion conditions.

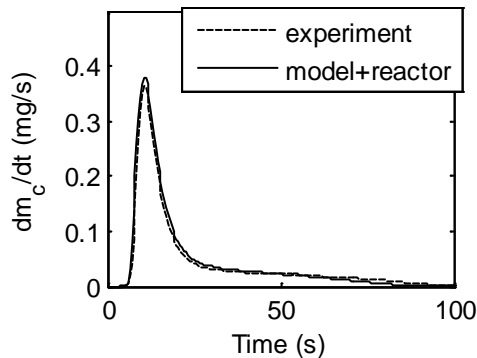


Fig. 1. Measured and modeled particle carbon release profile: $T_\infty = 800$ °C, $m_{particle} = 10$ mg, $f_{water} = 7$ %

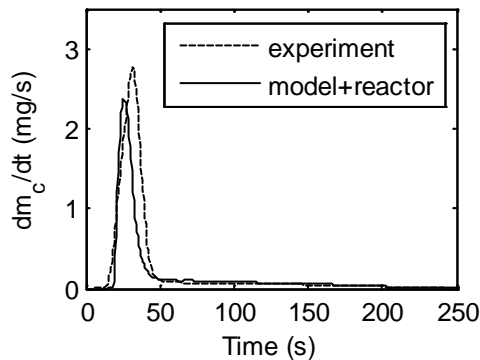


Fig. 2. Measured and modeled particle carbon release profile: $T_\infty = 900$ °C, $m_{particle} = 180$ mg, $f_{water} = 50$ %

A recently suggested multivariable optimization approach has successfully been applied to fit modeled to experimental burnout profiles of biomass chars, bituminous coal chars and anthracite chars. Figure 3 shows a contour diagram of kinetic parameters of a char where the levels represent a fit between modeled and experimental burnout profiles. The diagram demonstrates the sensitivity of the kinetic parameters against the fit between modeled and experimental burnout profiles. Figure 4 plots modeled and experimental burnout profiles of a char.

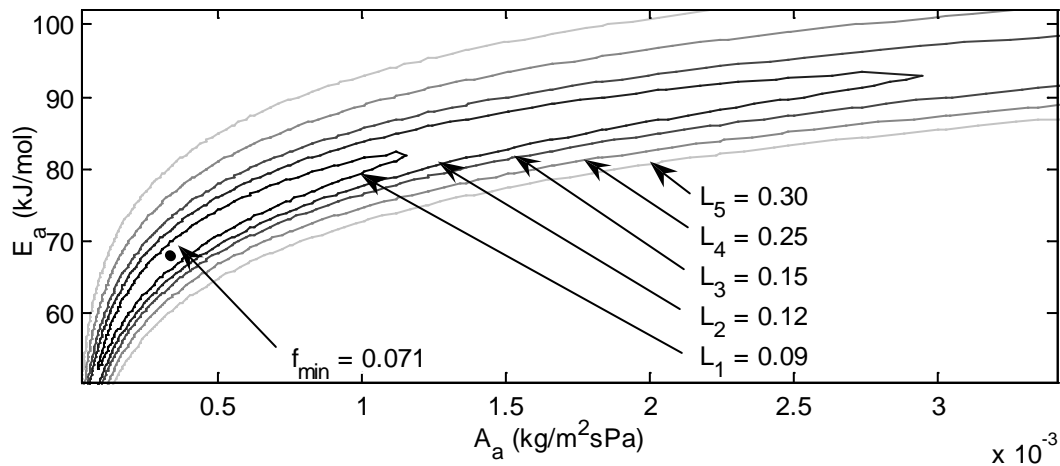


Fig.3 Contour diagram of pre-exponential factor and activation energy of South African coal. The values of the levels are included and represents the object function. The optimum apparent activation energy is marked (68 kJ/mol).

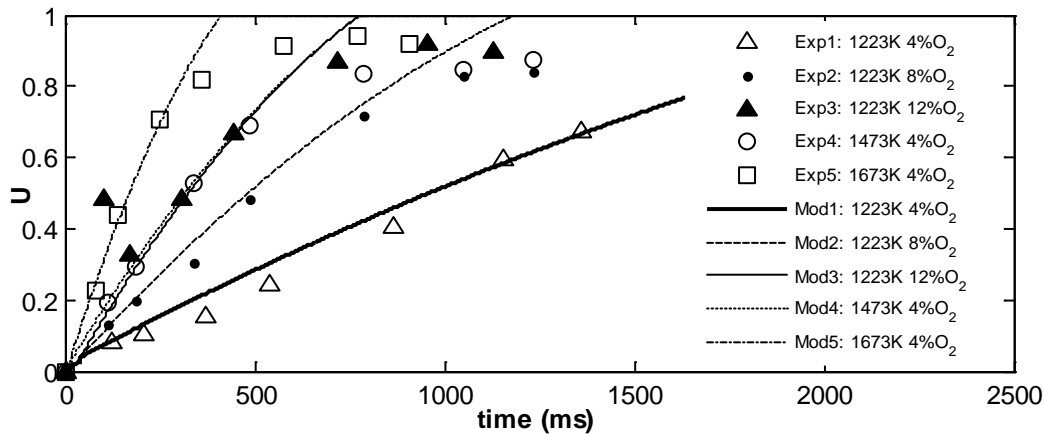


Fig.4. Modeled and experimental burnout versus residence time of South African coal char. Exp refers to experiment and Mod refers to model.

Fits of more than 20 chars demonstrate that the apparent reaction order is close to unity for biomass- and bituminous coal chars, while it is close to zero for anthracite chars at 1223 K. This is in contrast to much of the available literature, and important for CFD-modeling, since the value of the reaction order affects parameters such as kinetic parameters.

One recent study (O. Karlström, A. Brink, J. Hercog, M. Hupa, L. Tognotti. The 33rd International Symposium on Combustion. 1-6.8.2010) based on the optimization routines considered in this thesis showed that the apparent activation energies for 24 bituminous coal chars were relatively constant between 1223 K and 1673 K. This is surprising, since the apparent activation energy is a function of the internal surface area, and the surface area differs significantly for the 24 chars. Since most comprehensive CFD codes for modeling of pulverized fuel combustion are using simple kinetic/diffusion char models, these findings provide additional confidence in achieving predictivity, at least for the main combustion regions of the boiler where most of the heat is released by pulverized fuel. This is not the case for late stages of char oxidation that

should be treated by means of a more detailed and uncoupled post-processed approach to predict carbon in ash or mineral matter effects and transformations

Publications and Presentations:

O. Karlström, A. Brink, M. Hupa. "Analyzing fuel properties by a single particle furnace – combination of modeling and measurements". Scandinavian-Nordic Section of the Combustion Institute Topical Meeting: Measuring Techniques in Combustion, Gothenburg, Chalmers University of Technology 23-24.10.2008

A. Brink, O. Karlström, M. Hupa. A simplified model for the behaviour of large biomass particles in the splashing zone of a bubbling bed. 20th International Conference on Fluidized Bed Combustion, Xi'an, China 18-20.5.2009

O. Karlström, A. Brink, M. Hupa, L. Tognotti. "Kinetic combustion parameters for chars using the IFRF solid fuel data base". 16th International International Flame Research Foundation Members Conference, Boston. 8-10.6.2009.

O. Karlström, A. Brink, M. Hupa, L. Tognotti. "Modeling the combustion of coal chars in a drop tube using constant activation energy". Joint meeting of the Scandinavian-nordic and French sections of the combustion institute, Snekersten (Copenhagen). 9-10.11.2009

O. Karlström, A. Brink, M. Hupa, L. Tognotti. "Modeling the combustion of bituminous coal chars in a drop tube using constant activation energy". EDF-IFRF coal characterization workshop, Paris. 23.11.2009

O. Karlström, A. Brink, J. Hercog, M. Hupa, L. Tognotti. "Oxidation model for 24 bituminous coal chars: constant of variable activation energy". The 33rd International Symposium on Combustion. Tsinghua University, Beijing, China, 1-6.8.2010

Participation in GS biofuel courses

Analytical Techniques in Combustion Part 1, Gothenburg, 20-24.10.2008 (Nordic BiofuelsGS-2)

Analytical Techniques in Combustion Part 2, Copenhagen, 2- 6.2.2009 (Nordic BiofuelsGS-2)

Analytical Techniques in Combustion Part 3, Trondheim, 4-7.5.2009 (Nordic BiofuelsGS-2)

Analytical Techniques in Combustion Part 4, Turku, 21-25.9.2009 (Nordic BiofuelsGS-2)

Travelling

6.6.2008 IFRF solid fuel data base meeting, Livorno, Italy

17-18.2008 Solid fuel data base workshop, TUM, Germany

14-16.9.2008 Nordic BiofuelsGS-2 annual meeting, Visby, Sweden

8-10.6.2009 16th International International Flame Research Foundation Members Conference, Boston

14-16.6.2009 Nordic BiofuelsGS-2 annual seminar, Trondheim

9-10.11.2009 Joint meeting of the Scandinavian-nordic and French sections of the combustion institute, Snekkersten (Copenhagen).
23.11.2009 EDF-IFRF coal characterization workshop, Paris.
1-6.8.2010 The 33rd International Symposium on Combustion. Tsinghua University, Beijing, China
26-28.9.2010 Nordic BiofuelsGS-2 – Annual Seminar. Copenhagen, Denmark.

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TOPIC **Experimental testing of new flame
retardants in polymers**

MAIN SUBJECT **Inorganic chemistry**
SUPERVISORS Dr Anders Brink,
 Professor Mikko Hupa
M.Sc. March 2004
LICENTIATE STUDIES
Started January 2007
To be completed December 2010

Experimental testing of new flame retardants in polymers

Johan Lindholm

Background

Flame retardants are additives in products and materials to reduce the risk of fire. These additives delay, inhibit and prevent fires in different ways. For our safety, the use of flame retardants has increased during the last decades to finally be present almost everywhere, from electronic equipment to furniture, and the need is growing. Halogenated flame retardants have been widely used due to their high efficiency and low cost. Recently it has been proven that several of the halogenated flame retardants are carcinogenic bio-accumulative substances, and have then been banned by the EU. The clear benefits of prevented and reduced fires must not be equalled by negative effects of toxic chemicals.

The EU decisions, RoHS and WEEE directives have forced the polymer industry to find new alternatives and develop environmentally friendly non-hazardous flame retardants. Regulations and laws on flame retardancy and allowed flame retardants can differ from one country to the other. The new EU legislation for Registration, Evaluation, and Authorization of Chemicals (REACH) requires industry to provide data to establish the safety of new and existing chemicals.

When developing efficient new environmentally friendly flame retardants testing is needed. Many countries have different testing standards. One of the aims of this work is to develop a useful toolbox for testing new flame retardants in polymers using different techniques. To do this, existing equipment will be used and new equipment will be installed, tested and used.

Objectives

1. To develop test methods for evaluating the flammability of polymers.
2. To apply the methods to support the development of new fire retardants.
3. To study the physico-chemical mechanisms responsible for the effects of fire retardants.

Methods

- UL 94 standard testing (Figure 1)
- Cone Calorimeter (Figure 2)
- Video combustion
- DSC-TGA

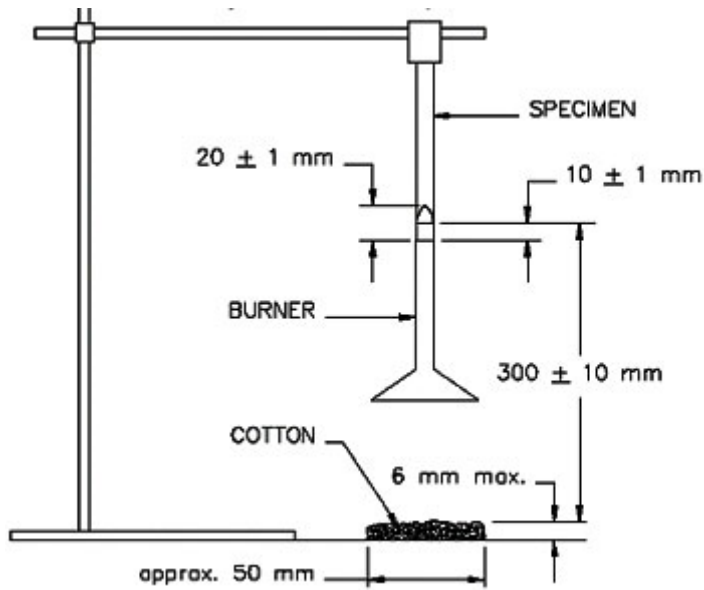


Figure 1. Schematic picture of UL 94 testing with vertical sample orientation.

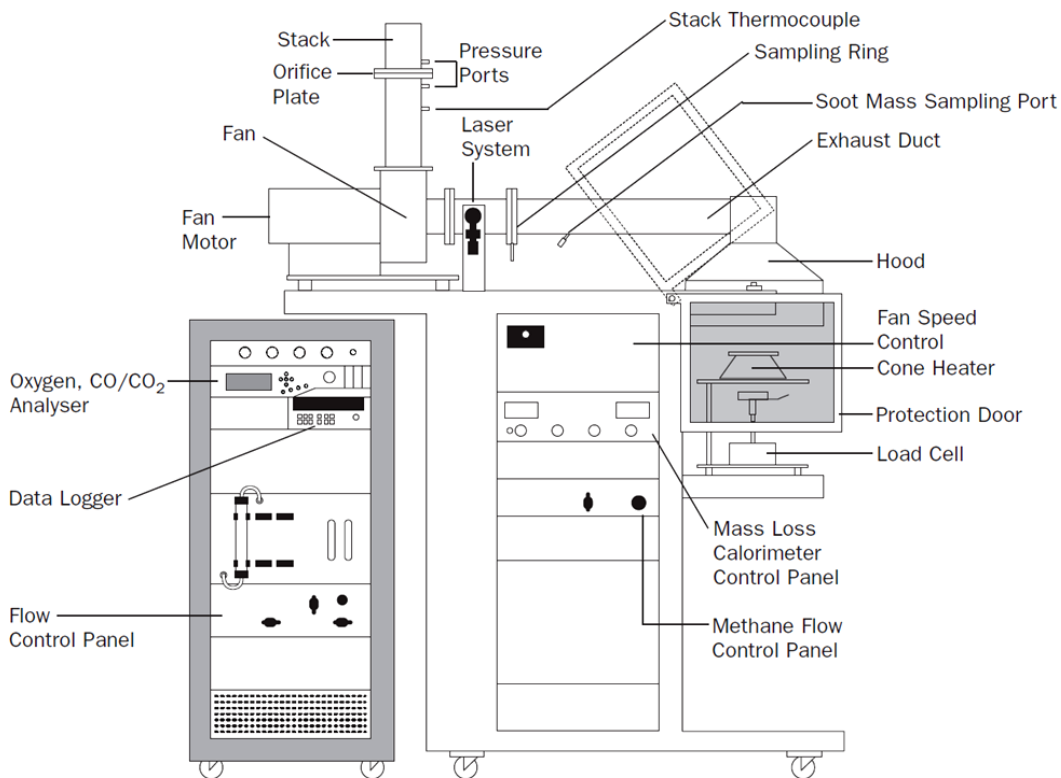


Figure 2. Schematic picture of a Cone Calorimeter.

Activities and Results

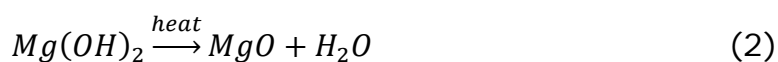
A UL 94 testing device and a Cone Calorimeter have been successfully installed and used for testing fire properties of various materials. Flammability properties, e.g. ignition and self extinguishing tendency of a material exposed to a methane flame, can be tested with the UL 94 testing device, a standardized method for testing plastic materials used in devices and appliances. Time-to-ignition (tti) and heat release rate

(HRR), among other parameters in the ISO 5660 standard, can be tested under forced flaming conditions in the Cone Calorimeter. The testing devices are shown in Figures 1 and 2.

The UL 94 technique showed good result reproducibility. Five series of flame retarded polypropylene samples were tested in vertical orientation. Each sample series consisted of 5 samples. A comparison between test results from two laboratories show some differences in the burning times. However, the classifications are the same. The standard deviations were very small which indicate stability between the experiments, even if the method is claimed to be operator sensitive.

Several different types of experiments were performed in the Cone Calorimeter for different purposes. To facilitate the testing of novel compounds synthesized in laboratory-scale, the possibilities to decrease the standard Cone Calorimeter sample size was investigated. Polypropylene (PP) wax, wood and polyurethane (PUR) adhesive samples were tested in decreased sample sizes. The samples were 50 and 25 % of the size prescribed in the standards. The peak heat release rate was found to be independent of the sample size for slow burning materials, indicating downscalability.

PUR adhesive samples were also modified with various inorganic additives in order to decrease their flammability and heat release. Several inorganic compounds with low melting point and release of incombustible gases during thermal decomposition were tested. For example different chlorides, hydroxides, phosphates were tested. The Cone Calorimeter results show that a delay in tti and a decrease in peak HRR can be achieved by various additives. Chrystal water molecules bound to the inorganic compound introduced a delay in tti. Especially sodium metasilicate pentahydrate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) was effective. The pure adhesive manufactured according to unchanged recipe ignited roughly 45 seconds after the start of the experiment, and a 20% addition of sodium metasilicate doubled the time. This effect comes from the water molecules that are released according to reaction (1). An addition of the same amount of magnesium dihydroxide ($\text{Mg}(\text{OH})_2$) radically decreased the peak HRR, from 270 to 200 kW/m^2 . $\text{Mg}(\text{OH})_2$ decomposes to release water and form MgO when heated, according to reaction (2). The results from the Cone Calorimeter experiments are shown in Figure 3.



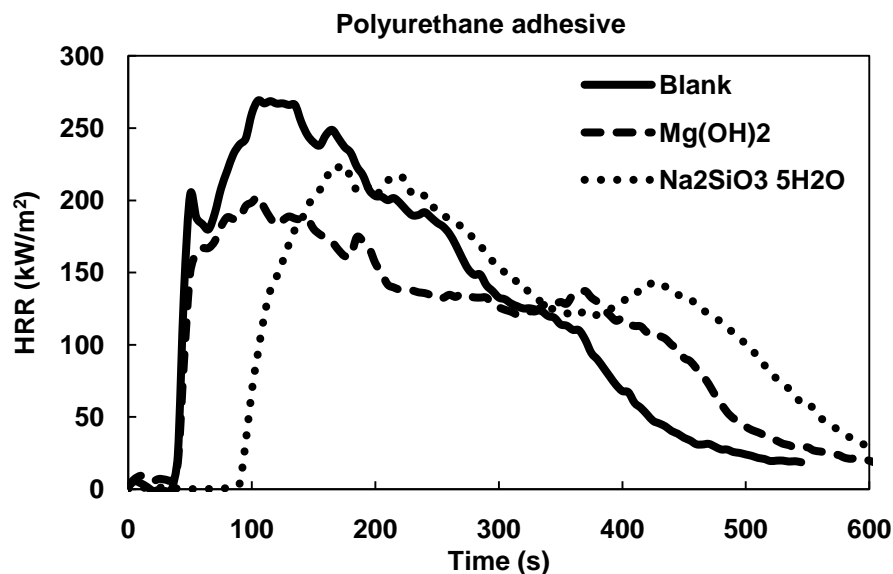


Figure 3. Cone Calorimeter results of PUR adhesive samples with magnesium dihydroxide and sodium metasilicate pentahydrate addition.

Thermogravimetric analysis was used to confirm melting and decomposition of the inorganic compounds used as flame retardants. The crystal water in the $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ is released in 3 steps, while $\text{Mg}(\text{OH})_2$ decomposes in one step. The theoretical mass loss should be 43 and 31%, respectively. The decomposition of the two compounds occurs at different temperature intervals, as can be seen in Figure 4, which shows results from thermogravimetric experiments. $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ has released all its water when the temperature reaches 250 °C. $\text{Mg}(\text{OH})_2$ starts to decompose at this temperature, and finishes at roughly 400 °C.

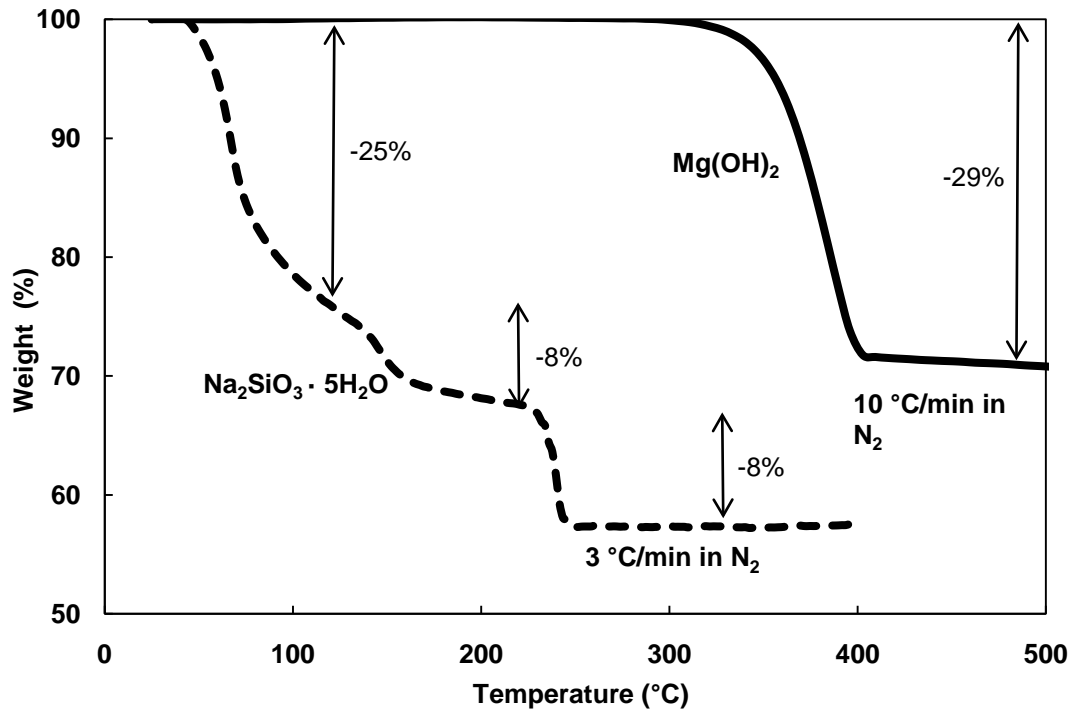


Figure 4. Thermogravimetric analysis in nitrogen atmosphere of sodium metasilicate pentahydrate and magnesium dihydroxide.

Additionally, video combustion was tested for PP and PP wax samples in the beginning of the project. This interesting visual combustion testing method did not suit the sample types tested.

Inorganic compounds melting at low temperatures or decomposing to incombustible species at relatively low temperatures can be used as flame retardants. By using different techniques to study the phenomena caused by the flame retarding inorganic additives, different effects can be seen.

Travelling and courses:

- 30.1.-2.2.2007 Course: Kraft recovery boilers - principles and practise. TKK⁴, Esbo, Finland
- 21.-25.5.2007 Course: Biofuels. TKK, Esbo, Finland
- 5.-6.11.2007 SNCI⁵, 4th Biennial Meeting. Åbo, Finland, presentation & extended abstract
- 19.-23.11.2007 Course: Thermochemical conversion of solid biomass and waste. CTH⁶, Göteborg, Sweden
- 30.1.-1.2.2008 Course: Waste to Energy and Recovered Materials from Waste. TKK, Esbo, Finland
- 9.-10.4.2008 KETJU⁷ Annual Seminar. Palace Kämp, Helsingfors, Finland, presentation
- 14.-16.9.2008 Nordic BiofuelsGS-2 Annual Seminar. Visby, Sweden, presentation
- 20.-24.10.2008 Course: Analytical techniques in combustion, Part 1. CTH, Göteborg, Sweden
- 23.-24.10.2008 SNCI, 6th Topical Meeting. Göteborg, Sweden, presentation
- 28.-29.1.2009 IFRF⁸ Finnish-Swedish Flame Days. Nådendal, Finland, presentation & paper
- 2.-6.2.2009 Course: Analytical techniques in combustion, Part 2. DTU⁹, Köpenhamn, Denmark
- 10.-11.2.2009 KETJU Annual Seminar. Sveaborg, Helsingfors, Finland, presentation
- 4.-7.5.2009 Course: Analytical techniques in combustion, Part 3. NTNU¹⁰, Trondheim, Norway
- 14.-16.6.2009 Nordic BiofuelsGS-2 Annual Seminar. Inderøy, Norway, presentation
- 21.-25.9.2009 Course: Analytical techniques in combustion, Part 4. ÅÅ¹¹, Åbo, Finland
- 19.-23.19.2009 ChemCom 2.0 boiler measurement campaign. Raumo, Finland
- 14.1.2010 IFRF V Liekkipäivä. Otnäs, Esbo, Finland
- 20.3.-3.4.2010 Giral Lignite Power Limited boiler measurement campaign. Rajasthan, India

⁴ Helsinki University of Technology

⁵ Scandinavian–Nordic Section of the Combustion Institute

⁶ Chalmers University of Technology

⁷ Academy of Finland Research Programme on Sustainable Production and Products

⁸ International Flame Research Foundation

⁹ Technical University of Denmark

¹⁰ Norwegian University of Science and Technology

¹¹ Åbo Akademi University

- 7.9.2010 KETJU Annual Seminar. Finlands Akademi, Helsingfors, Finland, abstract & poster
- 26.-28.9.2010 Nordic BiofuelsGS-2 Annual Seminar. Köpenhamn, Denmark, presentation

Publications and Presentations:

Johan Lindholm: "Experimental testing of new flame retardants in polymers". Åbo Akademi Process Chemistry Centre Annual Meeting, August, **2007**.

Johan Lindholm, Anders Brink, Mikko Hupa and Mélanie Aubert, Carl-Eric Wilén: "Reproducibility of the UL 94 flammability test of flame retarded polypropylene samples". SNCI, 4th Biennial Meeting, **2007**, Åbo, Finland.

Johan Lindholm, Mélanie Aubert: "Design of novel non-halogenated flame retardants". KETJU Annual Seminar, **2008**, Helsingfors, Finland.

Johan Lindholm: "Cone Calorimeter – A tool for measuring heat release rate". SNCI, 6th Topical Meeting, Measuring Techniques in Combustion, **2008**, Göteborg, Sweden.

Johan Lindholm, Anders Brink, Mikko Hupa: "Flame retardant research at Åbo Akademi University" & "Cone Calorimeter – A tool for measuring heat release rate". IFRF Finnish-Swedish Flame Days, **2009**, Nådendal, Finland.

Johan Lindholm, Mélanie Aubert: "Design of novel non-halogenated flame retardants". KETJU Annual Seminar, **2009**, Helsingfors, Finland.

Johan Lindholm, Anders Brink, Mikko Hupa: "Influence of decreased sample size on cone calorimeter results". Manuscript submitted to *Fire and Materials*, **2010**.

Johan Lindholm: "Cone Calorimeter - Combustion researcher entering fire research". Åbo Akademi Process Chemistry Centre Annual Meeting, August, **2010**.

Melanie Aubert, Johan Lindholm, Weronika Pawelec, Teija Tirri, Rafiehalsadat Norouzian Amiri, Anders Brink, Mikko Hupa, Carl-Eric Wilén: "Design of novel non-halogenated flame retardants – combustion and polymer scientists join forces". KETJU Annual Seminar, **2010**, Helsingfors, Finland.

Johan Lindholm, Anders Brink, Mikko Hupa: "Flame retarding effects of some inorganic compounds in polyurethane adhesive" (working title). To be submitted, **2010**.

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TOPIC

Ablative Flash Pyrolysis of Straw

MAIN SUBJECT

Flash Pyrolysis of Straw in Situ

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M.Sc.

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DOCTORAL STUDIES

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TOPIC	Thermal conversion of biomass with emphasis on product distribution, reaction kinetics and sulfur abatement.
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MAIN SUBJECT	Thermal conversion
SUPERVISORS	Prof. Johan Hustad Doc. Morten Grønli
M.Sc.	Dec 1997
DOCTORAL STUDIES	
Started	March 2004
To be completed	May 2009



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Research TOPIC

**Application of fly ash from solid fuel
combustion in concrete**

MAIN SUBJECT

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Research TOPIC **High temperature filtration**

MAIN SUBJECT **High temperature filtration in biomass
combustion and gasification processes**

SUPERVISORS Prof. Johan Hustad
Prof. Otto Sønju

M.Sc. July 2004

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Started August 2004

To be completed August 2008



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TOPIC **A laboratory method for studying high temperature corrosion caused by alkali salts**

MAIN SUBJECT **Inorganic Chemistry**

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Prof. Mikko Hupa

M.Sc. February 2002

LICENCIATE STUDIES

Started February 2005

To be completed September 2007