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## Fuel Quality Impact in a Historical Perspective: A Review of 25 Years of EU-Funded Research on Fuel Characterization, Ash and Deposit Formation, and Corrosion

Jappe Frandsen, Flemming; Fendt, Sebastian ; Spliethoff, Hartmut

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## Bioefficiency:

# A Continuation of 20 Years of EU-Funded Research on Fuel Characterization, Ash and Deposit Formation, and Corrosion

Flemming J. Frandsen<sup>1</sup>, Sebastian Fendt<sup>2</sup>, Hartmut Spliethoff<sup>2</sup>

<sup>a)</sup> *Technical University of Denmark (DTU), DTU Chemical and Biochemical Engineering, P. Søtofts Plads, DTU Building 229, DK-2800 Lyngby, DENMARK, +(45)45252883, [ff@kt.dtu.dk](mailto:ff@kt.dtu.dk)*

<sup>b)</sup> *Institute of Energy Systems, Boltzmannstrasse 15, 85748 Garching, Germany*

Heating and cooling are responsible for approximately half of EU's final energy demand, while biomass is currently responsible for more than 90% of all renewable heat. The goal is to increase share of biomass-based technologies, in the European heat market, from 11% in 2007 to about 25% in 2020 [RHC-Platform, 2014]. Combined Heat and Power (CHP) from biomass is a suitable technology for medium- and large-scale units, where many utility and industrial applications can be found, especially in Scandinavia. The main challenge for efficient CHP and high temperature steam production from biomass are ash-related problems. Corrosion due to the difficult ash composition of biomass limits both steam temperature and efficiency. By solving these issues, large-scale boilers offer a huge potential for efficiency increase and emission reduction, during CHP generation at cost-competitive and environmental friendly conditions. In order to reach these goals, and to enable a secure and nearly carbon neutral heat and power generation, recently, the **Bioefficiency** proposal, was granted under Horizon2020, aiming to:

- **Develop next generation, biomass-fired CHP plant**, increasing the steam temperatures up to 600°C, at medium to large scale (10 to 200 MWth).
- **Increase the efficiency of CHP plants** by elevated steam temperatures through solving and understanding of ash-related problems – slagging, fouling and corrosion.
- **Reduce emissions** – i.e. CO<sub>2</sub>, particulates, CO, NO<sub>x</sub>, and SO<sub>2</sub> – by efficiency gain, reduction of impurities and by intelligent plant design.
- **Broaden the feedstocks for pulverized fuel (PF) and fluidized bed (FB) power plants**, using pre-treatment methods with focus on the reduction of harmful, inorganic elements: Cl, S and the alkali metals.
- **Prevent power plant damage due to high-temperature Cl-induced corrosion.**
- **Reduce costs for utilities** due to increased efficiency, lowered emissions and fuel consumption, decreased number of outages and maintenance due to handling of ash-related problems.

- **Optimize biomass blending** (e.g. wood & sewage sludge) in order to reduce slagging, fouling and corrosion propensities by the adjustment of ash chemistry, enabling new ash utilisation options.
- **Develop better furnace materials.**
- **Widen ash utilization and nutrient recirculation**, by detailed ash analysis in terms of chemistry and physical properties.

When preparing the proposal, a state-of-the-art note on the above issues was written, and this paper contains a brief outline of the previous EU-based activities on these issues, which led to the outline and formulation of the Bioefficiency proposal. A complete review of 20 years of EU-funded research on fuel characterization, ash and deposit formation, corrosion, ash utilization is out of the scope, since it would require a substantial number of pages and details, but the paper serves more like a resume of the activities and, perhaps, a forerunner for a more detailed peer-view paper on this issue.

**Keywords:** EU-funded research, fuel characterization, ash and deposit formation, corrosion

## 1. Introduction

The inorganic (incombustible) fraction of solid fuels (which is naturally present, or sometimes added to the fuel, during handling or processing), may cause several problems during combustion, most importantly formation of particulate matter (aerosols and fly ashes), causing deposit formation (slagging and fouling) on superheater tubes. Deposits may in turn leads to a reduction in the heat transfer efficiency to the water/steam system, and, may cause to corrosion of superheater tubes. These problems may cause costly shutdowns of combustion units.

There are several studies on the chemical composition and the form of inorganic elements in biomasses [Zevenhoven et al., 2012, Werkelin et al., 2010, and Marschner, 2002]. The classification is based on the work of [Benson and Holm, 1985], who pioneered in this area and differentiate between the following occurrences of inorganic elements, in low ranked fuels:

- **Soluble salts** which originate from liquid phases, inside the plants. These elements are detected by washing in water or ammonium acetate. Elements found are cations such as  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$  and anions  $Cl^-$ ,  $HPO_4^{2-}$ ,  $H_2PO_4^-$ ,  $SO_4^{2-}$  or  $Si(OH)_3O^-$ .
- **Organically bound ash-forming elements** in the form of ion-exchangeable metal ions. Typical cations involve  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mn^{2+}$ ,  $Mg^{2+}$ ,  $Fe^{3+}$  and  $Al^{3+}$ . A further group consists of organically associated covalently bonded non-metals such as organic S, P or Cl.
- **Included minerals**, most commonly inside complex, organic molecules. Typical elements are Ca, Si and Fe, where e.g. Ca is frequently found in the form of calcium oxalate ( $CaC_2O_4$ ) which forms crystals during drying of biomass, typical for wood-based biomass. Another type is soluble Si in the form of silicic acid, which enriches in insoluble  $SiO_2$  within the cell walls, which is often found in straw.
- **Excluded minerals**, are mainly impurities such as soil or contaminants attached to the plant. They are mainly introduced in the feedstock through harvesting or processing. Typical representatives are clay minerals in the form of aluminosilicates, feldspars or quartz.

The main route between a burning fuel particle in a furnace and a troublesome deposit on a heat transfer surface, can be divided into a number of consecutive steps:

- **Release of critical ash-forming elements** (mainly K, Na, S, Cl, Zn, and Pb) during devolatilization, pyrolysis, and subsequent char burnout;
- **Formation of aerosol particles** by nucleation and coagulation of flame-volatilized ash-forming elements, and, formation **and entrainment of residual ash** (during char burnout);
- **Transport of ash species** i.e. gases, liquids (droplets) and solids (particles), from bulk gas to heat transfer surfaces and adhesion of these ash species to heat transfer surfaces, and;
- **Build-up, sintering (consolidation) and shedding of deposits.**

Concerning fly ash formation, early ash formation models focused on coal as a feedstock, where included and excluded minerals are dominating. The work of [Helble and Sarofim, 1989] resulted in a comprehensive understanding of ash formation, which is illustrated in Figure 1. The main ash formation mechanisms shown in Figure 1, and commonly mentioned in literature, are:

- Melting and fusion (coalescence) of mineral inclusions or excluded inorganic material
- Fragmentation of remaining char particles
- Shedding of ash particles from the char surface
- Homogeneous condensation (nucleation and coagulation/agglomeration) forming aerosols
- Heterogeneous condensation of inorganic vapours on existing ash particles

Fly ash formation is well described for coal-firing in suspension, where reliable models for prediction of final chemistry and particle size distribution have been published and tested, while for utilization of other fuels, the physical description of how the residual ash is formed is unknown territory, basically. The physical development of fly ash links strongly to the fate of this ash further down the line in the actual combustion system;

- Will it be lifted from the fuel-bed ?;
- Will it be transported to the heat transfer surfaces, and in case yes, where will that happen ?;
- Will it stick to a heat transfer surface upon impact ? and,
- How will it transform and/or interact with e.g. gaseous species during transport up through the freeboard etc. ?

Inorganic vapors from release of critical ash-forming elements, form submicron ash particles (often referred to as aerosols) via homogeneous condensation during the decrease in temperature inside the boiler. Particles are the in the size range of 0.1  $\mu\text{m}$ . A lot of focus has been but on aerosol formation mainly via a significant number of measuring campaigns reported in the literature. A good qualitative image and understanding of mechanisms of aerosol formation exists, and for some fuels 1<sup>st</sup> generation models for aerosols formation, transport and deposition have been suggested, but there is a big gap to step over, before these models are fully implemented in e.g. models for freeboard chemistry or advanced flow in furnaces.

The fine particles generated in biomass combustion are chemically characterised, mainly, by the elements K, Na, Cl, and S and are formed by condensation of volatile vapours [e.g. Christensen and Livbjerg, 1996; Nielsen et al., 1996; Zeuthen et al., 2007; Wiinikka et al., 2007]. Typically, these fine particles are composed of sulphates, chlorides or carbonates of alkali metals such as  $\text{K}_2\text{SO}_4$ ,  $\text{KCl}$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{CaO}$  and heavy metal compounds Pb, Cd, Zn, which can be found as tracers in the fuel. The

fine particulates are difficult to separate from the flue gas and one of the major emissions from biomass combustion. Particles can interact during the cooling of the flue gas forming larger agglomerates in the range from 0.1 to 1.0  $\mu\text{m}$ .

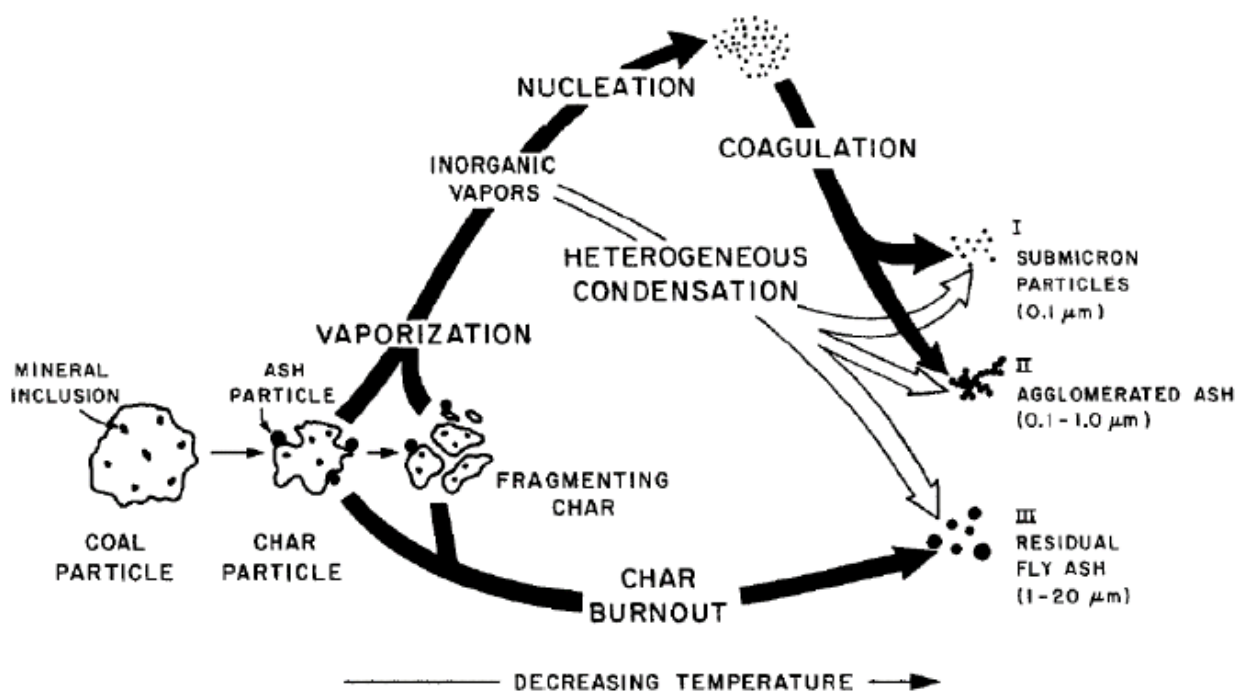


Fig. 1: Ash formation mechanisms during coal combustion [Helble and Sarofim, 1989].

The ash and aerosol formation mechanisms for coal and biomass are basically the same, however the amount of inorganics which vaporizes, is strongly increased for biomass. This is caused by a relatively high share of organically bound inorganics and salts, in the fuel matrix of plants. In addition, the vaporization depends on the time-temperature history of the fuel particle during the combustion. Higher residence times and temperatures lead to a higher share of inorganic elements vaporized. Typical values for different solid fuels are:

- Coal: 5-15 wt.-%: depending on the coal rank; dominated by alkali metals, S and Cl.
- Wood: 50-90 wt.-%: Ca, Mg, Mn, P, Ti, and Na, K, Cl, S, Zn: 80-100 % release.
- Straw: 30-50 wt.-%: Na, K, Cl, and Cl, S, Zn: 80-100 % release.

The behaviour of aerosols is important to the environment, and in relation to the public health. Traffic, wood stoves, power plants (i.e. heat and power production), and natural sources (e.g. dust, sea salt, and volcanic dust) are major sources of airborne particles [Friedlander, 2000]. Recent studies have shown that fine particles, defined as those with  $d_p < 2,5 \mu\text{m}$ , possess a great impact on visibility, health, and water droplet formation in the atmosphere [Zeuthen, 2007]. Epidemiological evidence correlates the increase in particulate matter (PM) mass concentrations with cardiopulmonary disease and mortality. No specific particles property or component responsible for the toxicological effects has yet been identified. However, the importance of particle properties other than mass concentration, i.e. the chemical composition, particle size, and number concentration, have been emphasised as very important [Lighty et al., 2000].

During the early Joule, FP5, FP6 and FP7, several R&D-projects, like OPTEB [EU-OPTEB, 1998], Deposit Prediction [EU-Deposit Prediction, 2001], BioAerosol [EU-BioAerosol2, 2003], BioAsh [EU-BioAsh, 2006], ToMeRed [EU-ToMeRed, 2004], BioCard [EU-BioCard, 2008], BRISK [EU-BRISK, 2016] etc., with focus on ash and deposit formation have been funded, internationally and nationally. Focus was often on grate or fixed-bed combustion with low efficiencies or on co-firing. Research in FB and PF combustion of 100% biomass is needed. In basically all these projects there had been a strong focus on experimental work in lab-, pilot- and full-scale, often collection gas, ash and deposit samples, and characterizing these chemically. This gives a strong indication of the elemental chemistry in ashes and deposits, as the chemical analyses were always provided on either elemental or oxide base. In addition, aerosol measurements and characterization, as well as studies of the release of critical ash forming elements like K, Na, S and Cl, from different types of biomasses were conducted.

## 2. Pre-Treatment of Biofuels

One option to reduce the threat of ash deposition and high-temperature corrosion, is by upgrading the feedstock with pre-treatment technologies, for which various treatments have been investigated, including;

- Torrefaction
- Hydrothermal carbonisation (HTC)
- Steam explosion

All three technologies recently received much attention, see Table 1, due to the improved characteristics of the product. For the energetic exploitation of biomass, pre-treatment technologies have proven to be crucial to address biomass-related difficulties, such as low energy density, degradation during storage and the lower energy consumption during grinding. However, investigations are mainly carried out in lab-scale, and for high quality fuels, such as wood. In addition, the fate of ash forming elements are often not investigated or characterized.

The torrefaction process involves the heating of biomass in inert atmospheres to temperatures of up to 350°C. This leads to mild pyrolysis processes, and the embrittlement of the material. Removal of oxygen from the fuel structure by devolatilisation and destruction of hemi-cellulose, improves the specific energy content, and reduces the mechanical stability of the fuel structure [van der Stelt et al., 2011] which results in an improved grindability and a simplified usage of torrefied biomasses in PF systems. The torrefaction technology recently has seen high industrial activity conducted by the International Biomass Torrefaction Council (IBTC), with pilot plants from 10 – 110 kt/a capacity being developed [Koppejan et al., 2012].

Large-scale implementation and firing of pellets, still lacks experience, however. First large scale research was conducted within the EU-funded project SECTOR, where firing of torrefied pellets was successfully implemented, in wood-pellet boilers. Regarding the fate of S, Cl, K and Na, first researches reported that with the transformation of the fuel structure and the release of volatile contents, a benefit on the fly ash formation and the corrosion potential can be achieved, via removal of volatile Cl and on a small level by internal transformation of S-species to volatile products [Saleh et al., 2014, Shoulaifar et al., 2013]. Here, the largest mitigation potential is offered by the removal of Cl by selecting optimized torrefaction conditions [Chen et al., 2016].

Due to its large potential of enabling and simplifying the use of sustainable energy sources and the capability for large-scale implementation the torrefaction process is currently optimized. The ongoing EU-projects SteamBio and INFRES focus on superheated steam torrefaction and implementation of infrastructures for large-scale supply of forest biomass. The lack of removal of low melting soluble ash contents like potassium is met by a combination washing and torrefaction and is implemented by ECN in the TORWASH project.

The HTC process requires immersion in water and heating to 180°C – 280°C with the water kept liquid and the fuels are transformed to a lignite-like product via removal of oxygen rich compounds by hydrolysis, decarboxylation and condensation reactions yielding a product with high heating value, high brittleness and a lower drying effort. A removal of soluble and low melting ash compounds and a reduction of corrosion/fouling potential could be shown in first studies [Reza et al., 2013]. Given the short timeframe in which HTC has received serious scientific attention, recent efforts in HTC were limited to lab- and pilot-scale experiments. Combustion as well as gasification behaviour is still subject to fundamental research mainly due to a shortage of available HTC-fuel for larger combustion setups. Industrial process implementation is currently under development on national levels, e.g. Suncoal (Carbo-Ren process), AVA-CO<sub>2</sub>, TerraNova Energy, Ingelia S.L.

*Table 1: Overview of EU-funded projects dealing with pre-treatment technologies for biomass.*

Project:	Bioefficiency partners:	Content:	Keywords:
BIONORM (ENK6-CT-2001-00556) Completion: 31.12.2004	DONG, ECN, NTUA	Development of standardized procedure for solid biofuel characterization	Solid biofuels, standard, fuel characteristics
SECTOR (282826) Completion: 30.06.2015	ECN, VTT	Pilot-plant production of torrefied pellets, development of standards	Torrefaction, standard, broad biomass feedstock
BRISK (284498) Completion: 30.09.2016	ABO, DTU, ECN, TUM	Network for production of biofuels	Biofuels, network, database
MOBILE FLIP (637020) Ongoing	VTT	Industrial processing of biomass for pre-treatment	Pelletizing, torrefaction, hydrothermal power

Steam Explosion is an innovative physico-chemical pre-treatment method for lignocellulosic biomass by an explosive release of high temperature steam after a short exposure time. The lignocellulose structure is disrupted by the rapid steam expansion and lignin compounds are removed exposing the cellulose to further processing in e.g. bioethanol processes or usage as dissolving pulp [Singh et al., 2015]. However, this pre-treatment method offers an innovative and cost efficient approach on upgrading residual biomasses to high quality fuels. Important research on combining steam explosion pre-treatment with the upgrading of solid fuels is still missing regarding the removal of inorganic compounds in the liquid phase. Furthermore, a heat integration concept with a CHP plant is missing.

### 3. Ash and Deposit Formation in Boilers

Through several years, high quality research have been conducted both in national and EU-funded projects, in order to characterize fuels, ashes and deposit formation in utility boilers fired with coal, biomass and waste fractions, see Table 2. Huge amounts of experimental data has been gained, from this work, but the fact is that there are still in 2016, a number of big gaps in our current understanding

of these phenomena, and that we need focus on these points, in order to be able to describe, understand and quantify the process of deposit formation completely.

A lot of focus has been put on detailed chemical and physical characterization of biofuels, e.g. in the Deposit Prediction, BioFlam, BioAerosols and BioAsh EU-projects, see Table 2. Such information is of utmost importance in order to link the fuel feedstock chemistry to fly ash, aerosol and deposit chemistry in thermal fuel conversion systems.

High-quality data are available on the release of critical ash-forming elements, although most of the lab-scale measurements are performed under experimental conditions different from what happens in full-scale. Several factors are known to influence the release and retention of elements and ash species during combustion of solid fuels [Senior and Flagan, 1982; Flagan and Seinfeld, 1988; Knudsen et al., 2004a,b; van Lith et al., 2006, 2008; Novakovic et al., 2009];

- First of all, the combustion temperature correlates strongly with the fraction of critical ash-forming elements (K, Na, S, Cl, Pb, and Zn) released.
- Secondly, *in coal combustion* the release of ash has been shown to be affected significantly by the oxidizing/reducing conditions during thermal conversion of the coal particles. The reducing conditions e.g. inside burning coal particles, may increase the vaporization of certain ash-forming elements, since the reduced form (sub oxide) of many oxides of ash forming elements have higher vapor pressures than the oxides.
- Third, the fuel composition affects the release. For biomass fuels several composition-dependent relations have been identified.
- Fourth, the fuel particle size and structure and temperature-residence time history affect the measured release rates.

Both the HiAl and BioAsh projects, see Table 2, contributed with new pioneering data on release, as well as with a substantial improvement in the understanding of release mechanisms serving as a link between biofuel chemistry and fly ash and aerosol chemistry.

Fly ash formation has through several decades been intensively studied for coal combustion, where the fly ash size distribution has a multi-modal size distribution, see Figure 2. The larger particles originate from mineral grains in the coal and their size distribution depends upon the coal characteristics, pre-treatment (sizing) of the coal, and, the actual combustion conditions. The submicron particles on the contrary, originate mainly from homogeneous nucleation, and subsequent coagulation of flame-volatilized inorganic species, see Figure 2. Other important processes going on include fragmentation of chars and mineral inclusions as well as coalescence of ash droplets on receding char surfaces.

The residual ash formed during thermal conversion of fuels may be further subdivided into bottom ash and fly ash, in a ratio depending mainly on fuel characteristics, furnace design, and size and density of the residual ash particles. In grate-fired units, the major part of the residual ash ends up as bottom ash (app. 70-95%) whereas in pc/pf-fired boilers, fly ash constitutes the main part of the residual ash (80-95%).

The fly ash is entrained by the flue gas through the flue gas channel, where it may deposit on heat transfer surfaces. The flue gas is cooled as it passes through the boiler; i.e. the gas may become supersaturated, and e.g. alkali species may condense, either heterogeneously on fly ash particles, or on heat transfer surfaces, or, homogeneously, as submicron (aerosol) particles.



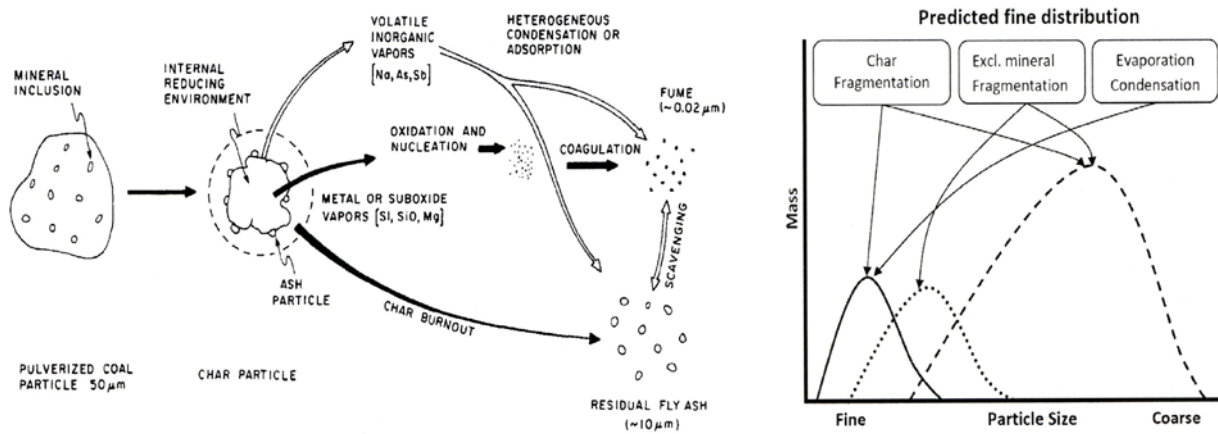


Fig. 2: Major transformation routes and transformation processes from a burning solid fuel to a fly ash particle size distribution. Source: [Haynes et al., 1982].

Concerning flame-volatilized, critical ash-forming elements [Christensen et al., 1998, 2000] investigated aerosol formation during straw combustion. The aerosol particles sampled in full-scale consisted of KCl and K<sub>2</sub>SO<sub>4</sub>, with KCl being dominant, but K<sub>2</sub>SO<sub>4</sub> being present in the core of the particles, see Figure 17. A quenched equilibrium theory by which the KCl, K<sub>2</sub>SO<sub>4</sub>, HCl, and SO<sub>2</sub> is determined by the equilibrium sulfation of KCl at 812 ± 10 °C, was used to quantify the chemical composition of the aerosol particles, and [HCl] and [SO<sub>2</sub>] in the flue gas. The authors suggested that aerosol formation is initiated by homogeneous nucleation of K<sub>2</sub>SO<sub>4</sub>, particles then grow by heterogeneous condensation of K<sub>2</sub>SO<sub>4</sub> and KCl. Aerosol formation in grate fired units, utilizing different grades of wood fuels were thoroughly addressed in the BioAerosol and BioAsh projects, see Figure 3.

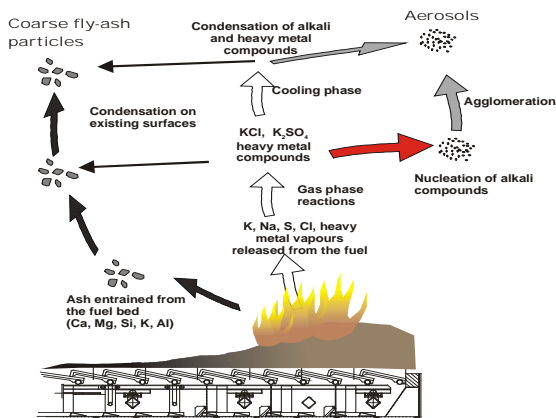


Fig. 3: Mechanism of aerosol formation as suggested by [Christensen and Livbjerg, 1996; Christensen et al., 1998] for straw-fired systems and by [Brunner et al., 2000, 2002] for wood chips fired systems. Source: [Brunner et al., 2000, 2002].

Ash particles entrained on the flue gas can cause a number of serious operational problems. Inside the boiler, ash particles and inorganic vapors can deposit on heat exchanging surfaces leading to an insulating layer. These deposits decrease heat transfer rates and thus steam generation and overall plant efficiency. In severe cases, power plants have to be shut down and cleaned which has a huge impact on economics. In addition, the power plant start-up involves oil-firing decreasing the sustainability. Ash deposition is mainly caused, by the following mechanisms [Frandsen, 2011]:

- Inertial impaction including eddy impaction on the tube rear
- Thermophoresis
- Diffusion of inorganic vapours leading to heterogeneous condensation and chemical reactions

*Table 2: Overview of EU-funded projects dealing with ash and deposit formation.*

Project:	Bioefficiency partners:	Content:	Keywords:
DepPred (JOR3-CT98-0198) Completion date: 30.06.2001	DTU, ABO, ECN, MHPSE	Deposit measurements and prediction, physical data	Deposition, probes, model, stickiness, viscosity
BioFlam (ENK5-CT-1999-00004) Completion date: 28.02.2003	DTU, NTUA, ECN, MHPSE	Fuel characterization	Biofuels, blends, physical and chemical data
EU-BIOAEROSOLS (ERK6/CT1999/00003) Completion: 28.02.2003	ABO, DTU	Measurements and modeling of aerosol formation in fixed-bed combustion, aerosol removal	Fixed bed combustion, aerosols, fly ash, deposits
HIAL (ENK5-CT-2001-00517) Completion: 30.11.2004	DONG, DTU	Release of alkali metals, S, Cl during biomass combustion	Grate-firing, release of species, corrosion, SO <sub>2</sub>
ToMeRed (ENK5-CT-2002-00699) Completion: 31.12.2016	ABO, DTU, ECN, MHPSE	Reduction of toxic metal emissions (Pb, Cr, Cd, Hg) during biomass-co-firing	Toxic metal emissions, Hg, co-firing, sorbents
BioAsh (SES-CT-2003-502679) Completion: 28.02.2006	ABO, DTU, ECN	Measurement and modeling of aerosol formation in grate firing and PF co-firing, deposits and corrosion	Grate firing, fine particles, corrosion, deposit, emissions
BioCard (SES6-2005-019829) Completion: 30.06.2008	DTU	Global process to improve Cynara Cardunculus utilization	Grate firing, FB, deposition, corrosion
CleanSelective (RFRC-CT-2006-00008)	ECN, TUM	Intelligent monitoring and selective cleaning of deposits in a PF system	PF system, deposition monitoring, selective cleaning
Enercorn (239476) Completion: 30.11.2013	DTU, VTT	Superheater corrosion, problems with wood and corn stover blends solved by ferric sulfate addition	Grate combustion, additives, superheater corrosion, ash melting

The dominant mechanism is inertial impaction, when a large, high inertia particle cannot follow the streamlines around a superheater tube. The particle will impact on the surface and depending on its stickiness, adhere and form an insulating layer. The particle will also deposit, if the surface itself is sticky, due e.g. to condensation of vapours forming a molten layer or deposition of small fly ash particles by thermophoresis. A temperature gradient in the boundary layer leads to a force on the particle which is referred to as thermophoresis. Ash deposition was heavily addressed in e.g. the Deposit Prediction, BioAsh and BioCard EU-projects, while the consequences of release of critical ash-forming elements were investigated and mapped in details especially in the ToMeRed, BioCard and Enercorn pEU-projects. Finally, the CleanSelective EU-project investigated means of intelligent monitoring and cleaning of deposits.

#### 4. Corrosion and Additives in Boilers

The extent of ash deposition and the deposit structure is mostly a function of the ash, its composition and melting behaviour. However, the amount of ash is also crucial and differs strongly between biomass types. Table 3 provides an overview on typical biomass fuels, typical combustion systems, maximum, currently achievable steam temperatures, the ash and chlorine content of fuels and the range of ash fusion temperatures. It can be seen that the Cl-content and ash melting temperature correlates with the maximum steam temperature. A lower Cl-content and higher ash melting temperature, result in higher steam temperatures and thereby increased plant efficiencies.

*Table 3: Overview of biomass combustions systems, their typical steam, temperatures, range of Cl- and ash-content, and ash fusion (melting) temperatures.*

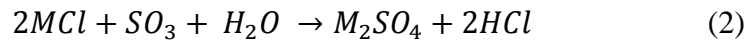
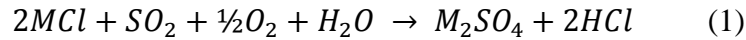
Fuel:	Firing system:	Max. steam temperature	Cl-content:	Ash-content:	Ash fusion temperatures:
% of thermal input	-	°C	mg/kg (dry)	% wt	°C
Straw (100)	Grate	540 (typical 450)	1000-7000	4,0-12	900-1300
MSW (100)	Grate	420	500-10000	10-40	1000-1300
SRF (100)	FB	470	900-15000	5-20	1000-1300
Wood chips (100)	Grate	500	50-100	1,0-2,5	1100-1400
Wood pellets (100)	FB/PF	< 540	50-150	0,1-2,5	1150-1500
Straw(15)/Coal(85)	PF	540	-	-	-
Sewage sludge (5)/coal(95)	PF	540	-	-	-
Waste wood	-	-	300-4000	3,0-12	1100-1300
Wood bark	-	-	100-370	5,0-8,0	1200-1500
Grass or hay	-	-	2500-20000	5-14	900-1350

The reason is the deposition of Cl, which has to be prevented under any circumstance. If for example solid KCl particles deposit, there is a severe risk of high-temperature Cl-induced corrosion. Gaseous chlorides in the flue gas cool down, condense on heat exchanging surfaces or to solid particles which can deposit due to thermophoresis. Inside the deposit, a sulfation occurs which liberates Cl<sub>2</sub> or HCl. The gas then migrates by diffusion to the tube wall where it can lead to eutectics with very low melting temperatures, e.g. 340 – 393°C in the KCl-FeCl<sub>2</sub> system. The so-called scale layer then oxidizes (oxide layer), and recycles chlorine to a long-lasting corrosion cycle, which can lead to corrosion rates of several mm/years. The mechanism itself and influencing parameters are still not fully understood and strongly depends on the temperature, the structure and chemistry of the deposit, the tube material and the surrounding gas composition and partial pressures. Chlorine induced corrosion and diagnosis of this, was dealt with e.g. in the CORRLOG- as well as in the OnCord-projects, see Table 4.

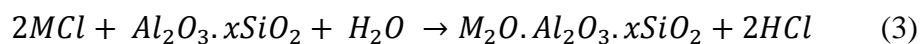
A quite popular corrosion mitigation strategy is to use high-sulphur containing fuels for the sulphation of alkali chlorides in the gas phase according to reaction (1) and (2). This has been studied in lab-scale [Iisa and Lu, 1999; Li et al., 2013] and full-scale applications [Zheng et al., 2007]. A reaction mechanism has been proposed for modelling purposes by [Glarborg and Marshall, 2005]. This is a useful tool for the modelling of the aerosol formation, as illustrated by [Hindiyarti et al., 2008]. [Robinson et al., 1998] found that if the molar S/Cl ratio is smaller than 2, one can expect high concentrations of chlorine in the deposit and thus high risk of high-temperature chlorine induced corrosion. For S/Cl > 4, very low Cl-contents were found in the deposit.

According to [Couch, 1994], important chemical reactions includes the formation of low melting eutectics by the interaction of inorganic elements inside the deposit, the oxidation, sulphation and the

absorption of alkali metals in aluminosilicates. They can occur between flue gas components such as SO<sub>2</sub>, SO<sub>3</sub>, H<sub>2</sub>O, O<sub>2</sub> and solids such as deposits or fly ash particles. The key reactions, often mentioned in literature are (1) and (2), where M represents alkali metals. Both reactions describe the sulphation of alkali chlorides to alkali sulphates, and the release of gaseous HCl:



The increased melting temperature of K<sub>2</sub>SO<sub>4</sub> compared to KCl leads to a lower share of sticky deposits [Frandsen, 2011]. A further important reaction, is the absorption of alkali species in the deposit, mainly attributed to aluminosilicates (3):



This absorption can lead to a formation of low-melting silicates. The transformation can include sintering, and may strongly affect physical properties of deposits, and the ability to clean heat exchanging surfaces, aspects that were addressed in the SLAGMOD-project, see Table 4.

However, high sulphur can lead to sulphur corrosion at higher temperatures. In addition, for pure biomass it is difficult to find feedstocks with sufficient sulphur content and sulphur leads to unwanted SO<sub>2</sub> emissions. Therefore, other strategies are popular among the biomass combustion community to prevent or minimize chlorine-induced corrosion. Often, additives are used to prevent the formation of alkali chlorides. Two main types are frequently reported, which are:

- Sulphur-based additives: chlorout (ammonium sulphate), ferric sulphate, pure sulphur
- Aluminosilicate-based additives: kaolin, coal fly ash, halloysite, clay minerals, zeolite, etc.

Recent effort to contribute to the understanding of the effects of additive insertion during biomass firing have been performed e.g. in EU-funded projects CORBI [54] and ENERCORN [55]. Further research was mainly funded by either power plant operators (e.g. Vattenfall, Dong Energy) or on a national level. An additive can also have a positive effect on the deposit structure and strength. The additive acts as a solid interface and reduces deposit strength which then lowers the cleaning effort. New developments aim to optimise the type, inserted amount and insertion technique of additives. A suitable additive should fulfil the following requirements: high reactivity, high thermal stability, cheap and easy to handle, and environmental-friendly with no disposal issue.

*Table 4: Overview of EU-funded projects dealing with corrosion and sensor development during solid fuel combustion.*

Project:	Bioefficiency partners:	Content:	Keywords:
CORRLOG (18207) Completion: 29.02.2008	DTU	Corrosion sensors as process control tools	Online corrosion monitoring, automation
SLAGMOD (ERK5-CT-1999-00009) Completion: 31.03.2003	ABO, NTUA	Online measurement and modeling of slagging and fouling during biomass combustion	Online slagging and fouling detection
OnCord (RFCR-CT-2014-00010) Completion: 30.09.2016	ABO, TUM, VAL, VTT	Testing and optimizing online corrosion sensors in co-firing applications, interact. of fuels	Online corrosion, monitoring, co-firing

## 5. Ash Utilization

Another very important issue is the utilization of biomass ash, which can be classified depending on the feedstock and/or the combustion system, and the position and technique where they are extracted from the flue gas. Typical locations can be bottom ash, cyclone ash, filter or electrostatic precipitator ash. The chemistry of biomass ash, strongly differs among feedstocks. Three main classes can be found:

- High silica, high potassium and low calcium ashes, with low fusion temperatures, including many agricultural residues and straw;
- Low silica, low potassium, high calcium ashes, with high fusion temperatures, including most woody materials, and;
- High calcium/high phosphorus ashes, with low fusion temperatures, including manures, sewage sludge, poultry litters or animal wastes.

EU waste management law is designed to protect human and environment. Thereby, an important aspect is the increased and sustainable utilization of resources. In order to achieve this goal, prevention, re-use, recycling and recovery are preferred over disposal. A product to which this law is applied to, are combustion residues. In case of coal combustion, avoiding the disposal of ashes is well approved in most European countries, and in 2008 only 7 % of residues have been disposed within the EU15 [Feuerborn, 2015]. In case of ashes from biomass combustion, utilization is not well established and the vast majority is still disposed. This fact can be proven by latest statistics from Austria; in-between 2010 and 2014 an average of more than 50 % of ashes from large-scale straw and wood combustion, have been disposed [BLFUW, 2015]. This situation is caused by different chemical and physical properties of ashes from coal and biomass combustion, whereby adaption of proven utilization paths is not possible. Depending on utilization option different chemical and physical properties are important. In the concrete industry, pozzolanic behavior and therefore the amount of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  are pivotal. Furthermore, an excess content of  $\text{SO}_3$  or  $\text{MgO}$  can lead to strength loss of the cement. Also the amount of unburned carbon has to be considered leading to reduced frost resistance. The chlorine content should be low in order to avoid corrosion issues in ferro-concrete applications. Concerning utilization as fertilizer amount of nutrients e.g. P, K, N as well as amount of potential hazardous heavy metals and their leaching behavior as well as pH value and therefore Ca content are relevant. Particle size distribution and density are of general importance for the utilisation. A further big problem is the current situation in the ash utilisation legislation. Currently every country has its own legislation which differ extremely from each other. The extent of biomass ashes produced in the EU 27 in 2005, was roughly estimated to 5,6 million tons. To achieve the target of 20% renewables by 2020, even 15,5 million tons per year could be produced [Van Eijk et al., 2012]. Compared to about 100 million tonnes of coal ash among all European members in 2007, this is still a significant share [Feuerborn, 2015].

In order to improve the current situation, the GASASH project focused on the possible utilization of residues from biomass gasification, see Table 5. Different utilization and after-treatment options, including low-temperature combustion and thereby producing ashes similar to fly ashes from combustion, have been investigated. Although no universal solution has been found, approaches for the utilisation of specific ashes could be determined. Another project focusing on biomass ash utilisation is IEA founded Bioenergy Task 32. Within this project a general overview of possible utilisation options was developed. Furthermore, a database (BioBank) concentrating on composition of biomass ashes from grate furnace is presented. Additionally, Värmeforsks programme

“Environmental friendly use of ashes” and “Ash Program” focused on the utilisation of ashes from mainly biomass combustion. Among others utilisation in civil engineering, fertilizer production or in forest soils are investigated in detail. A further topic is the improvement of ash properties. The EU-funded project “fractionated heavy metal separation and ash utilisation in biomass combustion and gasification plants”, studied heavy metal behaviour and fractionation. Other projects such as POWERFLAM2 or DEBCO also investigated the utilisation of ashes but contrary to above-mentioned not with 100 % biomass, but with advanced co-firing of biomass and coal.

*Table 5: Overview of EU-funded projects dealing with ash utilization from biomass combustion.*

Project:	Bioefficiency partners:	Content:	Keywords:
GASASH (ENK5-CT-2002-00635) Completion: 31.10.2005	ECN	Ash utilization options and improvement of ashes in gasification applications	Biomass gasification, ash utilization, ash treatment
POWERFLAME2 (FP5-EESD) Completion: 31.12.2012	Laborelec	Biomass co-firing, ash quality and marketability	Biomass co-firing, ash marketability
DEBCO (FP7-ENERGY-2007-2-TREN) Completion: 31.12.2012	Laborelec	High-share biomass co-firing, with focus on effect on ash properties and utilization	Biomass co-firing, ash utilization

## 6. Summary and Conclusion

During the last 20 years, there was a lack of investigation of how the coarse ash is actually formed during thermal conversion of biomass. 30 years ago a pioneering model on fly ash formation in PC-fired units was released at MIT, a model that is now implemented in deposit simulators worldwide, and which was based on 25+ years of detailed investigation of coarse ash formation in pulverised coal-fired boilers. The fact is that this level of understanding for biomass thermal conversion does not exist at present. There is a lack of data on how the coarse ash is actually formed as a function of fuel, firing technology, residence time, oxygen level and feedstock particle size. Before this information will be gained, the modelling of fly ash formation is not possible, and thereby makes predictions of deposition propensities, independent of full-scale data. Today, most deposit simulators for biofuels are based on fly ash chemical and size distributional data, from measuring campaigns. Therefore, in this project, we focus strongly on the effect of pre-treatment and thermal conversion conditions on fly ash formation.

**Concerning deposits, there is a lack of understanding** of how e.g. sulfation goes on in mature in-boiler deposits, a process that will determine both the porosity, the sintering and the corrosive potential in this boilers. Bioefficiency will conduct full-scale deposition studies in a boiler firing biomass in suspension and combine these data with lab-scale studies of sulphation, thereby enlighten the effect of sulphation and take a significant step further towards understanding corrosion and sintering/shedding, in these boilers.

Further there is a lack of data on the exact speciation of the chemistry in ashes from thermal conversion of biofuels. Potassium, for example, does not appear in an ash or a deposit as either elemental K or the parent oxide, K<sub>2</sub>O, as is usually stated in the bulk ash chemical analyses. Potassium may appear as e.g. K-silicate, K<sub>2</sub>SO<sub>4</sub>, KCl, K<sub>2</sub>CO<sub>3</sub>, K<sub>3</sub>PO<sub>4</sub> or even in mixtures of these or other

chemical species. But there are almost no data available on this speciation, a fact that will also be addressed via advanced analyses, such as quantitative XRD [Frandsen, 2011]

**Bioefficiency** will also investigate the **chemical interaction of additives, untreated and pre-treated biomass fuels**, further. The goal is to optimise the effectiveness of the alkali capture in different firing systems and hence minimize the required amount. In addition, tests will be conducted in a drop tube, above the melting temperature of the additive, a region where mechanisms are not understood yet. This will contribute directly to reduced deposit built-up, the mitigation of corrosion problems and economic benefits due to reduced boiler outage times. Investigations in full-scale power plants will also use online corrosion sensors, which are currently developed in the EU-funded project OnCord coordinated by TUM. In addition, material tests are conducted in long-term exposure tests in different scales (lab- and full-scale) in order to improve the resistance for the formation of an oxide layer and find future alloys.

**Thermal pre-treatment technologies** are currently receiving much attention. However, though commercial technologies are available from a number of vendors, these technologies are still in a relatively lower TRL level, compared with the established purely mechanical pre-treatment, as for instance production of standardized white wood pellets. Further research is particularly needed for low-grade feedstocks and on the **fate and form of inorganic elements before and after the treatment**. This will also be addressed within Bioefficiency, the partners of which have a long history in this field, and will perform innovative biomass pre-treatment and the combustion, corrosion and deposition behavior of both, pre-treated and untreated fuels is studied. Another goal is to investigate the influence of washing via chemical fractionation. Furthermore, advanced fuel characterisation methods will be used to quantify ash forming elements – in particular S, Cl, K and Na – and their form.

**Bioefficiency** will focus on **improvement and development of ash utilisation** options by the **use data generated in the project** and of ash properties from existing databases. Thereby chemical and physical properties are not only dependent on the source of biomass but also to the combustion technology and the type of ash (bottom or fly ash). An approach to assign ashes with utilisation parts was developed by Vassilev et al. [11]. They classified ashes depending on main composition in four classes and six sub-types assigned with possible utilisation options. Figure 10 shows the classification system. Within Bioefficiency the classification system will be used and validated by ash database of Laborelec and the data generated in the project. Weakness of this classification system is, that physical properties such as leachability or trace elements like hazardous heavy metals are not considered, although these properties have a crucial impact on usability. Therefore, Bioefficiency will also introduce guidelines and restricts.

Furthermore, within a **specific biomass, differences in composition and properties** originate by planting environment, harvesting season, storage time or the part of biomass, resulting in unpredictable ash properties and thereby difficult utilisation [33]. Within Bioefficiency the influence of seasonal variation, storage and pre-treatment of ash properties is investigated in full-scale combustion with a special focus on impact on utilisation.

Besides technical and environmental problems there is also a lack of **technical regulation and legal situation in the European Union**, complicating the utilisation. Considering the utilisation as a fertilizer, different regulations and guidelines are applied. For instance a variation in restrictions on nutrients and heavy metals content. Some countries do not even have guidelines for the utilisation of

biomass ashes as fertilizer. For the utilisation in cement or construction material production no technical regulation is applied. European Guidelines EN 450-1 or EN 13055 developed for utilisation of coal combustion residues are not applicable for 100 % biomass combustion [70]. By comparing the current situation and regulation within the EU with respect to chemical and physical properties of ashes from full-scale combustion, Bioefficiency will contribute to develop new technical regulations for biomass ashes.

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