

Inorganic Species Behaviour in Thermochemical Processes for Energy Biomass Valorisation

K. Froment*, J.-M. Seiler, F. Defoort and S. Ravel

CEA Grenoble DRT/LITEN/DTBH/LTB, 17 rue des Martyrs, 38054 Grenoble Cedex - France
e-mail: karine.froment@cea.fr - jean-marie.seiler@cea.fr - francoise.defoort@cea.fr - serge.ravel@cea.fr

* Corresponding author

Résumé — Comportement des espèces inorganiques dans les procédés thermochimiques de valorisation énergétique de la biomasse — Les espèces inorganiques de la biomasse (bois, déchets agricoles, déchets ménagers voire boues d'épuration) présentent un large spectre en compositions et quantités, dépendant de l'origine de la biomasse (nature, lieux et conditions de sa croissance, etc.). Les différents procédés de conversion (combustion, pyrolyse, gazéification, etc.) et les différentes technologies associées (fours à grille, lits fixes ou fluidisés, réacteurs à flux entraînés, etc.) utilisant l'énergie de la biomasse, fournissent des conditions opératoires très variées en atmosphère, température, pression, etc. Au cours de chacun de ces procédés thermiques de conversion, en fonction de la composition initiale de la biomasse, de l'atmosphère et la température du procédé (la pression est un paramètre de second ordre par rapport aux précédents), certaines espèces inorganiques réagissent pour former des composés liquides ou gazeux, seuls ou combinés à d'autres espèces : celles-ci peuvent être soit piégées à différents endroits dans le procédé, soit relâchées avec le gaz. Les interactions potentielles de ces espèces inorganiques avec les parois des réacteurs, les matériaux de lits (en réacteurs à lits fluidisés), les canalisations et l'aval du procédé ne sont pas toujours bien connues.

Ces sujets concernant le comportement des espèces inorganiques et les conséquences technologiques et économiques vont probablement prendre de l'importance dans un futur proche en raison de :

- la tension sur le marché du bois qui augmente ainsi que les prix : une solution est de remplacer cette ressource « noble et propre » qu'est le bois par une ressource plus riche en cendres, comme la paille, les cultures énergétiques dédiées, ou les déchets agricoles voire ménagers. La production de biogaz depuis des décharges de déchets est une bonne illustration de la valorisation de déchets. Aller plus loin dans l'utilisation de ces ressources (conversion thermochimique) riches en cendres augmentera leur potentielle réutilisation mais également les difficultés techniques de manière importante !
- l'enrichissement des sols pour l'agriculture dépend aujourd'hui de la possibilité de réemploi des cendres de biomasse, auxquelles il faut ajouter des fertilisants artificiels. La question de comment réutiliser la matière inorganique de la biomasse après conversion thermochimique devient un sujet important.

L'objectif est de présenter une synthèse des difficultés technologiques liées à la présence de ces espèces inorganiques (corrosion, bouchages, etc.) : un résumé détaillé du comportement des espèces inorganiques de la biomasse dans les procédés thermiques sera donné, allant des espèces relâchées pendant le traitement de la biomasse jusqu'à la prévention et les solutions quand c'est possible. Les sujets suivants seront développés :

- inventaires des espèces inorganiques de différentes ressources ;
- synthèse de la spéciation des espèces inorganiques dans les divers procédés de conversion thermiques ;
- barrières technologiques à franchir pour des raisons économiques et améliorations technologiques des procédés à réaliser ;
- aspects particuliers liés au comportement des espèces inorganiques étudiés au CEA :
 - volatilisation et condensation des espèces inorganiques ;
 - comportement des aérosols et dépôts ;
 - filtration à chaud des particules ;
 - formation de laitier et interaction avec les parois des réacteurs.

Abstract — Inorganic Species Behaviour in Thermochemical Processes for Energy Biomass Valorisation — *Inorganic species from biomass (wood or agricultural waste) exhibit large variations in compositions and amounts, depending on the origin of the biomass (nature, growing conditions and location). Different thermal conversion processes (combustion, pyrolysis, gasification or other) and various technologies (grate furnace, fixed or fluidized bed, entrained flow reactor) using biomass, provide a wide variety of operating conditions with differences in atmosphere, pressure and temperature. During any thermal process and mainly depending on initial composition of the biomass, process temperature and atmosphere, some of the inorganic species react and may form liquid or gas compounds, alone or combined with other species: they may either be trapped at different locations during the process or released in the gas. The potential interactions of inorganic species with reactor walls, bed materials (in fluidized bed reactors), transfer lines and downstream process units are not well understood for most species.*

Both technical and economic issues about inorganic species behaviour are probably growing to become important in a near future:

- *pressure on timber markets is growing and prices have already been rising : one solution is to replace this noble and “clean” resource (wood) by ash richer feedstock, like straw, dedicated energetic cultures, agricultural or even municipal solid waste. Biogas production from waste deposits is a good example to show how waste can be valorised. Going further (thermochemical conversion) with such ash rich feedstock will increase the potential of their re-use but also the technical difficulties in a dramatic extent;*
- *soil enrichment for the agriculture currently largely depends on the re-use of biomass, completed with artificial fertilisers. The question how to re-use the inorganic material in biomass after thermo-chemical conversion is an important subject.*

The objective of this paper is to present a global review of the technological difficulties (corrosion, fouling, etc.): a detailed summary of the specific behaviour of the inorganic compounds in biomass thermal conversion facilities will be given, going from the description of inorganic species included in biomass up to the prevention and the solution, as far as possible. The following topics will therefore be developed:

- *inventory of inorganic species in different biomasses;*
- *general review of the inorganic speciation during thermal conversion processes;*
- *technological barriers to overcome for economic and technological process improvements;*
- *specific aspects related to inorganic species behaviour investigated at CEA:*
 - *inorganic species release and condensation;*
 - *aerosol behaviour and deposits;*
 - *hot particles filtration;*
 - *slag formation and interactions with reactor wall.*

INTRODUCTION

Inorganic species from biomass (wood or agricultural crops, waste) exhibit large variations in compositions and amounts, depending on the origin of the biomass

(nature, growing conditions and location). Different thermal conversion processes (combustion, pyrolysis and gasification) and various technologies (grate furnace, fixed or fluidised bed, entrained flow reactor)

converting biomass energy, are working under various operating conditions implying variations in the atmosphere, pressure, temperature, etc.

With increasing temperature, degradation reactions occur: organic matter is converted in gases and/or liquids of interest that can be used either directly to produce electricity and heat in turbines and motors, or in further synthesis steps (methanation, Fisher Tropsch synthesis for liquid biofuels, chemicals, etc.). At the same time, some of the inorganic species also react and may form solid, liquid or gas compounds. Once in the gas phase, these compounds may condense and be trapped at different locations all along the process. They also can be conveyed in the final gas, entrained out of the facility.

The potential consequences of inorganic species interactions with reactor walls, transfer lines and downstream processes are well known: corrosion, fouling, deactivation of catalysts, agglomeration of bed materials in fluidized beds but not all well understood. Some solutions to overcome the difficulties are known but they are quite expensive and CAPEX/OPEX of the facilities are then increased.

Both technical and economic issues about inorganic species are probably growing to importance in a near future:

- pressure on timber markets is growing and prices have already been rising: one solution is to replace this noble and “clean” resource (wood) by ash richer feedstock, like straw, dedicated energetic cultures, agricultural or even municipal solid waste. Biogas production from waste deposits is a good example to show how waste can be valorised. Going to thermochemical conversion with such ash rich feedstock will increase the potential of re-use but also dramatically increase the technical difficulties;
- soil enrichment for the agriculture currently largely depends on the re-use of biomass, completed with artificial fertilisers. The question how to re-use the inorganic material in biomass after thermo-chemical conversion is an important subject.

The objective of this paper is to present a global review of the technological difficulties (corrosion, fouling, etc.) and of the status of the art and studies that are going on about these issues. The specific behaviour of the inorganic compounds in biomass thermal conversion facilities will be discussed, including the inorganic species composition of biomass, the prevention of the risks and the solution, as far as possible. The following topics will therefore be developed:

- inventory of inorganic species in biomass;
- general review of the inorganic speciation during thermochemical conversion processes;
- technological barriers to overcome for economic and technologic improvements,

- specific aspects related to inorganic species behaviour investigated at CEA:
 - inorganic species release and condensation;
 - aerosol behaviour and deposits;
 - hot particles filtration;
 - slag formation and interactions with reactor wall.

1 THE INORGANIC SPECIES IN DIFFERENT FEEDSTOCK

The mineral part of biomass, also called biomass ashes, represents generally less than 1 wt% in wood, but can rise up to 8-10 wt% in straw, some agricultural wastes or in Short Rotation Coppice (SRC). Domestic waste contains much more mineral matter, and sludge can contain up to ~ 50 wt% inorganic matter.

Typical compositions for 3 main types of feedstock can be found in Table 1. The content in volatiles N, S, Cl, F and in metallic elements is usually presented in their elemental form. The “mineral” part of the ashes is usually presented in their oxide form even if the real chemical form might be more complex (oxide, carbonate, sulphates and others) (Vassilev *et al.*, 2012, 2013).

Even though the differences in organic elements C, H and O amounts are often limited, non-organic elements such as sulphur, chlorine, metals, etc., exhibit very different concentrations. Woody biomasses are calcium rich whereas straw are silica and potassium rich (Dupont *et al.*, 2010) and (Vassilev *et al.*, 2012). The ratio silica/lime and alkali content varies depending on type of biomass: for instance following SiO₂/CaO ratios are typically encountered: wheat straw (~8), miscanthus (~5), wood (~0.3).

Furthermore, for a same type of biomass, the mineral part of the biomass presents a large variation in composition depending on the growing conditions (soil, climate variations and harvesting (Dupont *et al.*, 2010)). It is obvious that, when heated at temperatures between 700 (typical for fluidized bed) and 1 400°C (typical for entrained flow reactor), most of these elements will react in different ways, forming a wide variety of species depending on the nature of the reactor atmosphere (oxidizing or reducing conditions), temperature and pressure but also on the existing materials in the near environment (bed, pipes, refractory materials, etc.).

2 INORGANIC SPECIATION DURING THERMAL CONVERSION PROCESSES

The objective of this paragraph is:

- to provide an overview of the species that can be released during the thermal treatment of biomass;

TABLE 1
Example of elementary compositions for typical feedstock taken from (Dupont *et al.*, 2010)

		Wheat straw	Miscanthus	Coniferous wood
H ₂ O	%	9.7	10.40	17.40
Ash 550°C	%dm	6.7	1.70	0.50
Ash 815°C	%dm	6	1.80	0.50
C	%dm	46.5	49.40	51.30
H	%dm	5.57	5.65	6.05
O (calculated)	%dm	41.45	43.04	42.10
N	%dm	0.48	0.11	< 0.01
S total	mg/kg	1 900	1 600.00	240.00
Cl total	mg/kg	700	500.00	340.00
F total	mg/kg	46	29.00	57.00
As	mg/kg	< 0.1	< 0.1	5.70
Pb	mg/kg	< 0.1	< 0.1	1.00
Cd	mg/kg	< 1	< 1	< 0.4
Cr	mg/kg	8	8.00	1.00
Cu	mg/kg	3	2.00	3.00
Ni	mg/kg	8	4.00	2.00
Hg	mg/kg	< 0.1	< 0.1	< 0.05
Zn	mg/kg	11	10.00	8.00
B	mg/kg	33	11.00	2.00
SiO ₂	wt% ash	58.3	55.60	10.80
Al ₂ O ₃	wt% ash	0.3	3.90	4.40
Fe ₂ O ₃	wt% ash	0.3	1.80	2.10
TiO ₂	wt% ash	< 0.1	0.30	0.40
CaO	wt% ash	7.1	10.70	32.40
MgO	wt% ash	1.8	4.00	9.90
K ₂ O	wt% ash	16.8	5.80	7.90
Na ₂ O	wt% ash	0.3	0.90	1.00
SO ₃	wt% ash	2.9	3.70	2.80
P ₂ O ₅	wt% ash	3	1.50	4.10
MnO ₂	wt% ash	0.2	0.20	1.70
<i>Total</i>	<i>wt% ash</i>	<i>91</i>	<i>88.40</i>	<i>77.50</i>

dm: dry matter.

- to identify the main elements and species that can be considered as problematic for the different components in various processes:
 - chlorides or sulphates that may cause corrosion;
 - species that condense in liquid or solid particles that may plug the pipes;
 - reactions leading to liquid phases in or with bed materials and may entrain bed agglomeration, etc.

Thermodynamic calculations can help to make predictions of speciation of all these elements depending on temperature and pressure, when the binary, ternary and other systems are described in the associated databases. For the other cases, it is possible to use SGTE (Scientific Group Thermodata Europe) databases, taking into account that some limitations remain as liquid and solid solutions are not described in that case.

The speciation of the inorganic elements depends mainly:

- on the temperature of the process, pressure dependency being generally of the second order;
- on the oxygen partial pressure (highest in combustion, low for gasification and pyrolysis);
- on the relative amount of the inorganic elements themselves.

Results are discussed element by element in the following for the nine main ones. These results are mainly derived from the literature, some of them are conclusions from own calculations. In the literature, available data are mainly focused:

- on combustion processes (with the related atmospheric pollution issue);
- on agglomeration in fluidized beds processes (but for combustion mainly, only few results are available for gasification);
- only very few results are available on volatility and/or condensation in gasification processes, particularly for high temperature processes (such as in entrained flow reactors).

2.1 Chlorine

Chlorine is found in the gas phase for any temperature. It is found as NaCl, KCl, and as HCl (Porbatzki *et al.*, 2011) if not enough K and Na are available in the gaseous phase. When the temperature is very high (about 1 400°C), thermodynamic calculations indicate that HCl concentration should increase but no measurements are found in the literature at elevated temperature (Gabra *et al.*, 2001; Petit, 2011).

2.2 Alkalines K, Na

For gasification or pyrolysis, K and Na release is strongly increased with temperature, 10 to 30 mol% release

at 750°C up to nearly 100% at 1 400°C according to thermodynamic calculations (Wei *et al.*, 2005; Gabra *et al.*, 2001). Measurements performed at 700 to 900°C are in disagreement with these calculations results (measured release are always smaller than calculated) (Mojtahedi *et al.*, 1990; Turn *et al.*, 1998) and no measurements are found in the literature at 1 400°C. The speciation is mainly as chlorides (Porbatzki *et al.*, 2011) as there is generally enough chlorine present but also as hydroxides when the oxygen partial pressure increases (Gabra *et al.*, 2001; Wei *et al.*, 2005; Petit, 2011).

In combustion processes, in presence of sulphur, K and Na sulphates are predominantly formed and stay solid. If there is no or little sulphur, K and Na carbonates and oxides can be found.

2.3 Sulphur

Sulphates are mainly formed in combustion, trapping many other elements (Na, K, Mg, Ca, etc.). These species stay in solid phase. However, when less oxygen is available, sulphur can be found as H₂S and COS or SO₂ (depending on oxygen partial pressure) up to 50 to 70% of S being released in the gas phase between 800 to 950°C (Van der drift *et al.*, 2001; Valin *et al.*, 2010). Knudsen *et al.* (2004), Ohman *et al.* (2005) and Petit (2011) confirmed that about 50% of the sulphur content can be released in the gas at about 800°C.

2.4 Nitrogen

Nitrogen can be in much larger amounts when air is used in the industrial process. N is mainly found in the gas phase, whatever the temperature and the atmosphere. In gasification, NH₃ and HCN can be measured, sometimes in very small quantities, hardly detectable for low N containing biomass such as wood. N release is directly proportional to N biomass content (Zhou *et al.*, 2000). NH₃ is the main gaseous specie measured (De Jong, 2005; Van der drift *et al.*, 2001), which appears to be in strong disagreement with thermodynamic equilibrium calculation results. This discrepancy is due to kinetic limitation (Kilpinen *et al.*, 1991). In combustion, NO_x can be formed, but have to be eliminated before combustion gas release in the environment.

2.5 Magnesium, Calcium, Silicon, Phosphorus

These elements generally stay in the solid phase, as oxides, sulphates or phosphates with Mg and Ca and silicates with Ca, K or Al (Vassilev *et al.*, 2012), even in gasification (Coda *et al.*, 2007).

At high temperatures ($\sim 1\ 400^\circ\text{C}$), silica rich slag containing iron oxides and alkali may be liquid. Phosphates MgP and CaP tend to decrease the melting temperature. Above 800°C to $1\ 000^\circ\text{C}$, CaCO_3 (calcium carbonate) and MgCO_3 decompose to CaO, MgO and CO_2 . Silica contributes to decrease the melting temperature for CaO rich ash and *vice-versa* and also contributes to increase the viscosity of molten ashes.

3 TECHNICAL BARRIERS TO OVERCOME

3.1 Interactions with Bed Materials

Agglomeration in fluidized beds is linked to the fact that the ash stays in the bed and, at 750°C and above, the mineral phases begin to melt. As the amount of ash increases *versus* time, the liquid fraction increases which can lead to bed agglomeration. Several publications deal with this issue, on the basis of analyses made after cool-down of the agglomerated bed material (Fryda *et al.*, 2008; Liliedahl and Sjöström, 1997; Zevenhoven-Onderwater *et al.*, 2001a,b; Wekerlin *et al.*, 2010; Kirnbauer *et al.*, 2011a,b).

The agglomeration process depends:

- on the ash composition, mainly on the concentration in low melting species (like Na_2O , K_2O , phosphates, etc.);
- on the liquid fraction associated with a considered ash at a given temperature level (the liquid fraction increases with the concentration of low melting materials);
- on the interactions with the bed material and on the purity of bed materials (dolomite, sand, olivine, etc.).

For instance, Na_2O , K_2O can form low temperature liquids and dissolve SiO_2 . The amount of liquid phase can increase by the dissolution of SiO_2 . Furthermore, the resulting liquid phase is viscous and sticky which promotes agglomeration of bed particles by the liquid phases.

Currently, some experimental studies provide empirical relationships between temperature, alkali concentration, ash accumulations, etc., beyond which there is a risk of agglomeration (Fryda *et al.*, 2008; Visser *et al.*, 2008; Ohman *et al.*, 2005). These models are valid for specific experiments but cannot be enlarged to other bed materials or a different temperature range. It is difficult to predict with a more general approach such interactions because the calculation of the liquid fractions is not very reliable due to incomplete thermodynamic data. These chemical systems are complex, and it is difficult to characterize the liquid phases existing at high temperatures.

The agglomeration phenomenon occurs necessarily but its importance depends on the kinetics, the operating duration, bed material and feedstock. When liquid amount is above a threshold, the sticking and agglomeration phenomena cannot be avoided, except if bed material extraction is performed.

Of course, it is obvious that high ashes containing feedstocks with high concentration of low melting temperature species are not suitable for fluidized beds technologies.

3.2 Behaviour of High Temperature Wall in an Entrained Flow Reactor

In an entrained flow reactor, the melting point of ash is reached. Molten ash is collected on reactor wall where it flows down and exits the reactor in the lower part.

The reactor wall is designed:

- as a high temperature barrier surrounding the reactor;
- as a heat resistant wall that minimizes the heat losses through this wall;
- as a slag collector.

One option, for small capacity reactors ($< \sim 1$ tonne/h), is to design a reactor wall that is formed of thick ceramic layers (10 to 20 cm). This technique obviously leads to a significant reduction of heat losses. But the ceramic material is corroded and even dissolved into the molten ash (slag). This leads to the necessity of the periodic replacement of the ceramic wall and maintenance costs.

The most important alternative, only suitable for high capacity reactors ($> \sim 1$ t/h), is to use an externally cooled wall with solidified ash forming the thermal insulation internal layer. This option leads to life times that are significantly longer but also to higher heat losses. In order to reduce the heat losses and also to limit the thickness of the solidified ash layer, the reactor operating temperature must be controlled in close connection to ash composition and properties. This will be discussed in a more detailed way below.

3.3 Heat Exchanger Corrosion

The species that leave the reactor in a gaseous form may condense at lower temperature, for instance in a heat exchanger, recovering heat from the high temperature gas.

It is well known that liquid KCl (as well as NaCl) corrodes very efficiently stainless steel which can lead to the destruction of the heat exchanger (and high maintenance costs). Depending on its partial pressure, KCl may condense below 700°C . Furthermore, KCl condenses in liquid phase at elevated pressure. Some metallic alloys,

like Hastelloys and Haynes steels (steel alloy with cobalt) exhibit an increased resistance to corrosion for temperatures up to $\sim 850^{\circ}\text{C}$.

Of course the condensation behaviour depends strongly on gas composition, pressure and temperature. The presence of particles in the gas (such as soot or fly-ash) affects the partition of the deposition between the wall and the particles.

Detailed condensation of different species is very difficult to predict with present knowledge. At best, the behaviour of some species that are recognized as harmful can be analyzed in some more details in order to prevent catastrophic failure of heat exchanger tubes. But other minor species may also have harmful action, even when they act slowly but that will only reveal faults after longer operation periods.

Condensation and corrosion are very complex problems that must be addressed and solved for specific applications.

3.4 Deactivation of Catalysts

Various processes associated with biomass thermochemical processes involve catalytic promoted reactions. Catalytic materials are generally sensitive to minor species. For instance, nickel is sensitive to sulphur. The reaction between Ni based catalyst and H_2S (from a gasification reactor) produces NiS at the surface of Ni particles. Surface deposition of NiS inhibits the catalytic effect of nickel.

Different catalysts are sensitive to different inorganic species. This imposes the necessity of gas cleaning before the catalytic reactors.

4 SPECIFIC ASPECTS RELATED TO INORGANIC SPECIES BEHAVIOUR

4.1 Inorganic Species Release and Condensation

Knowledge of inorganic species behaviour is a crucial issue due to their effects on the gasification and the downstream processes. Corrosion, agglomeration and catalyst poisoning can therefore influence strongly reactor design and the gas cleaning. Inorganics may also be a source of environmental concern (air pollution or slag recovery). It is important to know where they are produced and in which form (species). Thermodynamic equilibrium calculations have already been applied in literature for coal gasification and for some elements (N, Cl, S, alkali) in biomass gasification. They have apparently not been carried out for trace and other major inorganic elements for biomass. Furthermore,

comparison with experiments has not always been performed.

A dual approach (calculations and experiments) was used to study the fate of inorganics during steam gasification, for woody biomass (Froment *et al.*, 2013) and with a focus on alkali behaviour (Defoort *et al.*, 2012). They performed equilibrium calculations and characterisation of the gaseous and condensed phase at the exhaust of several equipment such as a bubbling fluidized bed linked to a high temperature gas reforming reactor (Valin *et al.*, 2009, 2010). Thermodynamic calculations were carried out with the FACTSAGE software and associated databases to simulate several biomass gasification processes (Bale *et al.*, 2009).

In the experiments, several on-line and off-line analyses and sampling were implemented in the facilities to measure gas phase compositions these include $\mu\text{GC-TCD}$ (micro-Gas Chromatography coupled with Thermal Conductivity Detectors) to follow, on line, sulphur containing species H_2S and COS or FTIR (Fourier Transform Infra Red spectroscopy) to analyse on-line water soluble inorganic species (NH_3 , HCN , HCl). Certain species (NH_3 , HCN , HCl , alkali) are also measured off line by ionic chromatography after being trapped at the exhaust of both facilities by washing bottle trains with several liquid solutions (Defoort *et al.*, 2010). Colorimetry for H_2S trace or mass spectrometry (*Airsense*) for tars and inorganics traces was also implemented.

For the condensed phase, inorganics were also measured off-line in the residue left in the fluidized bed and in deposits observed on candles and/or wall of the exhaust pipe by conventional chemical methods after dissolution or by SEM-EDX and XRD analysis.

4.1.1 Woody Biomass Volatility Results

The volatility and the condensation of 26 traces and major inorganic elements were calculated *versus* temperature, total pressure and for different gasification reactor technologies (Fluidized Bed, FB; Entrained Flow, EF) in allothermal or autothermal gasification conditions for woody biomass (Froment *et al.*, 2013). This work has been performed as part of the INORGANIC project partly funded by the French Research Council (ANR).

This work permitted to highlight the elements and their speciation that are calculated to be volatile, semi-volatile or entirely condensed, *versus* the working temperature (*Fig. 1*). The temperature is linked to the reactor technology.

Calculations were cross-checked with measurements from FB in the CEA facilities and from literature for steam gasification of woody biomass. Agreements with calculations were obtained for elemental mass balance

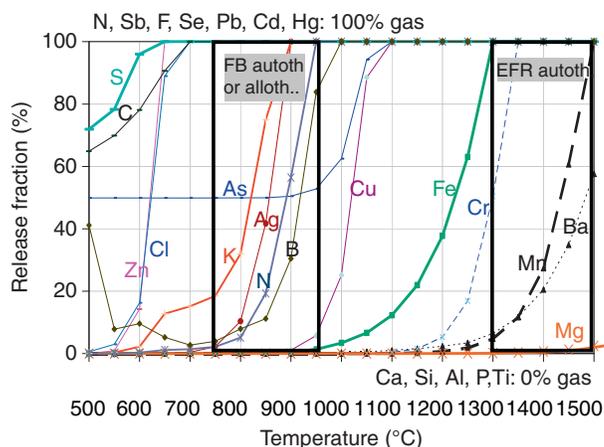


Figure 1

Elemental release fraction in the gaseous phase *versus* temperature, calculated at 1 bar, for EFR autothermal and for FB allothermal and autothermal wood gasification.

measurements of N, S, Cl classified as volatile and Al, Ca, Mg and Mn as condensed phases. Speciation of gas is calculated to be N_2 , H_2S , KOH and KCl with trace of HCl in agreement with explicit measurements for H_2S but not for N_2 (kinetic limitations (Kilpinen *et al.*, 1991)) and no quantitative conclusions for KOH, KCl and HCl. Cooling-down calculations predicted deposits of K_2CO_3 followed by KCl as the main condensate compounds without experimental comparison available for wood.

4.1.2 Alkali Volatility Results

With the same dual approach, alkali volatilisation of various biomasses representative of the feedstock diversity during steam gasification was studied (Defoort *et al.*, 2012). Eight different biomasses were gasified in the CEA fluidized bed as part of the AMAZONE Project partly funded by the ANR. Thermodynamic calculations predicted two different alkali volatilisation behaviours in the typical temperature range of fluidized bed.

For silica rich biomasses (Wheat Straw, Triticale and Miscanthus) the species in the gas phase are predicted to be mainly KCl and HCl (*Fig. 2*) and detailed calculations shows that the K/Cl molar ratio in the gas phase is lower than 1: this is in agreement with measurements (see left part of *Fig. 3*).

For silica poor biomasses (Calys, Coniferous wood, Short Rotation Coppice Poplar, Eucalyptus, Tall Fescue) the species in the gas phase are predicted to be mainly KCl and KOH (*Fig. 2*). The K/Cl molar ratio

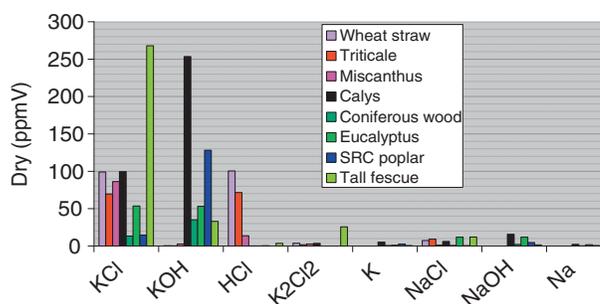


Figure 2

Composition of alkalis in the gas phase calculated at 850°C, given in volume concentration (in ppmV dry gas) for different feedstock.

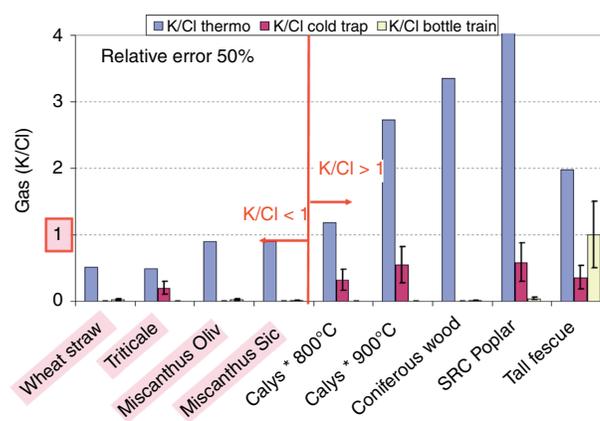


Figure 3

Measured and theoretical K/Cl molar ratio in gas phase.

in the gas phase should therefore be higher than 1. This is in disagreement with measurements (see right part of *Fig. 3*).

Further work is planned to improve this approach by using more sophisticated thermodynamic databases and new measurements for gas and condensed phases.

4.1.3 Conclusion

These results show the interest of using a dual approach (calculations and experiments) to study the fate of inorganics during gasification (even if there is still a large margin of progress in the understanding) and calculation of the speciation of potentially harmful components in the syngas.

It is noteworthy that in the EFR temperature range, no experimental release data for biomass gasification

are available in the literature to corroborate the calculations.

4.2 Aerosol Behaviour and Deposits in a Gasification Process

The work reported in this paragraph is performed as part of a PhD and a French research program (ANR SLUGAS): the objective is the analysis of inorganic species condensation in a biomass gasification facility. Final purpose is to better understand the way aerosols are produced and behave in the process both from experimental and modelling aspects.

A preliminary approach based on thermodynamic equilibrium calculations allowed to determine the nature and distribution of the inorganic species that can be volatilised during gasification, and to provide a guide to their speciation during gas cooling. It was concluded from this study that KCl is a good candidate to be used as a model species for vapour and aerosol formation in experiments.

Both experimental and modelling were performed (Petit *et al.*, 2012a,b):

- an experimental facility (ANACONDA) is designed and operated, in order to reproduce the main environmental conditions representative of a gasification facility (see Fig. 4): KCl vapour with graphite particles (simulating soot) are prepared in zone 1 and can be condensed with different cooling rates in zone 2. In zone 3, the gas and particles are quenched in a dilution probe, collected and analysed using an Electrical Low-Pressure Impactor (ELPI) and a Scanning Mobility Particle Sizer (SMPS);
- a modelling approach was developed for aerosols condensation, which takes place during syngas cool-down. The model is derived from the individual and analytical description of the different phenomena involved (nucleation, growing, agglomeration and deposits). The model is able to take into account the presence of precursor particles like soot. A simplified model was built, taking the global approach proposed by (Christensen *et al.*, 1998). This approach is developed using an *a priori* set of phenomenological models that had previously also been derived for biomass combustion: the model approach has been modified and adapted biomass gasification. The new model is validated against ANACONDA experimental results.

Measurements on the facility include: during the tests, external temperatures profiles along the reactor tube, concentration and granulometry of the input and output graphite and KCl particles by sampling on filters, and the granulometry distribution by ELPI measurements.

After the test, analysis of the filters samples allows to determine the morphology of the condensed particles and the mass balances.

4.2.1 Results

A cooling rate of 1 000 K/s was first applied with a gas flow rate of 30 L/mn. Different tests were performed.

As an example, some results on the influence of soot particles on condensation and wall deposits are given below.

Figure 5 shows the distribution of the collected particles size *versus* the measured characteristics by the ELPI (aerodynamic diameter), obtained in 4 different experiments:

- 2 reference tests; initial KCl particles or initial carbon particles are injected without evaporation: the result provides the reference mass distribution and the characteristic sizes of the initial solid particles;
- KCl particles are injected alone, without carbon, then heated and condensed: a very fine class of particles appears, resulting from homogeneous nucleation of KCl during cooling;
- KCl is injected with soot particles, then heated and condensed: a third maximum appears in the measured size distribution.

At the same time, the mass deposited at the wall is measured and given in Table 2: deposits seem to be influenced by graphite seeds; condensation on soot particles reduces the KCl wall deposit.

Modelling results confirm the observed tendencies. A validation of the model is obtained for the given experimental conditions. Work has to be continued to enlarge the validation for different cooling rates and aerosol mixture compositions. This global model, even if it is only partly validated, already allowed us to propose new solutions to minimise wall deposits and improve clean up of the syngas.

4.2.2 Conclusion

First results for a gas cooling rate of 1 000 K/s show an important kinetic limitation of particles growth leading to a nucleation peak when there are no graphite seeds. Very fine particles are nucleated that are difficult to filter. Seeding the flow with graphite particles reduces vapour deposition on wall and leads to larger particles that are easier to filter. Comparison between experimental results and calculations allows the validation of the modelling approach and a quantification of the relative weight of the different physical phenomena on the various condensation and deposition processes. Using this modelling

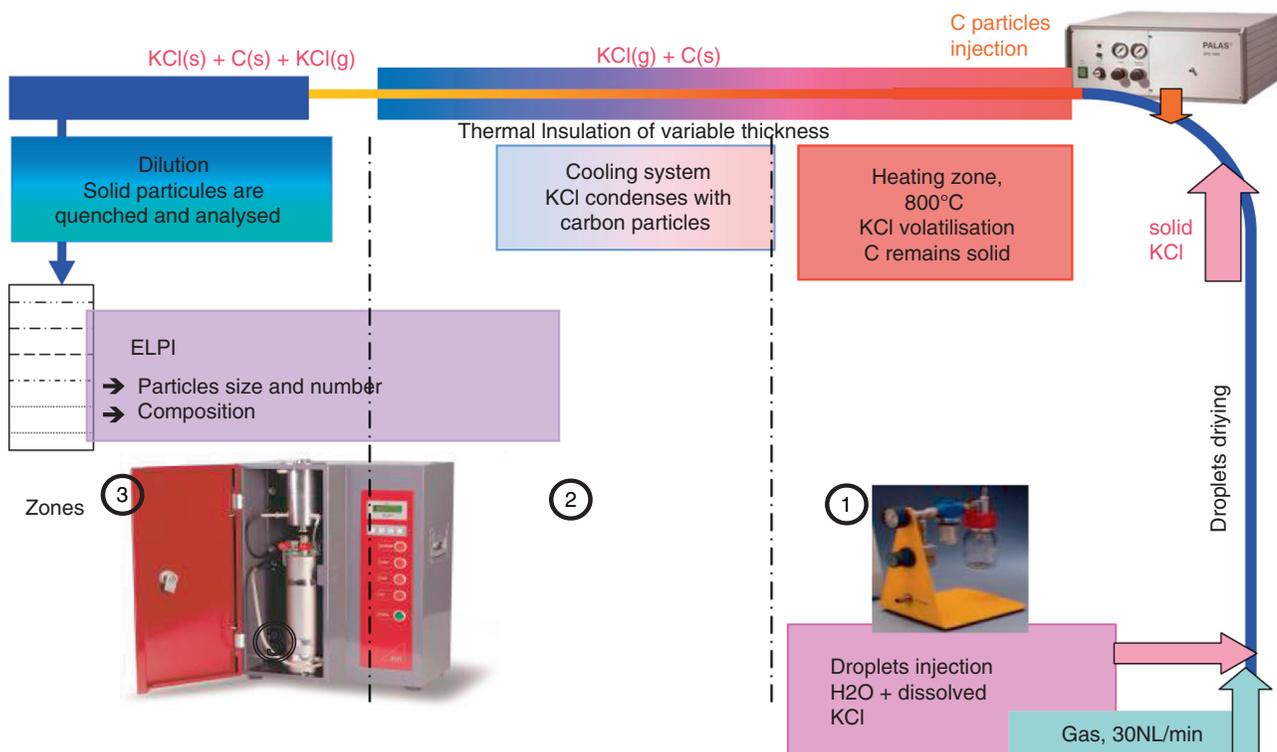


Figure 4
General diagram and working principle of the ANACONDA facility.

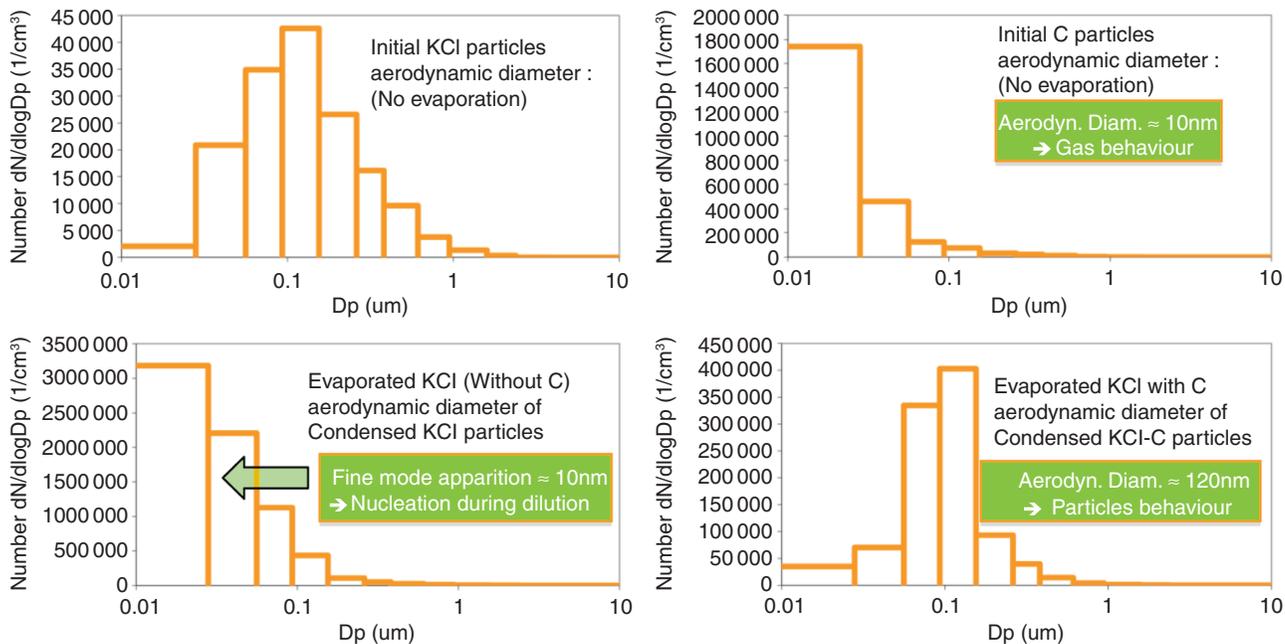


Figure 5
Experimental distribution of the collected particles during 4 different experiments.

TABLE 2
Influence of graphite seeds on wall deposits

Inlet	Test characteristics	Outlet mass concentration in the gas
Initial KCl 5 mg/m ³	Initial KCl particles (no evaporation)	4 mg/m ³ (20% deposit)
	Evaporated condensed KCl	1.7 mg/m ³ (65% deposit)
	Evaporated - condensed KCl with C	2.3 mg/m ³ (54% deposit)

tool for industrial applications allows solutions to be tested in order to prevent technological difficulties that are currently encountered.

4.3 Hot Particles Filtration

As part of other French research programs, hot particles filtration was examined in order to maintain as high as possible the syngas temperature for economic reasons. Candle filters, electrofiltration and thermophoretic filtration were tested, during the ANR projects called EPURGAS and THERMOCAPT.

4.3.1 Candle Filtration Results

Candle metallic and ceramic materials were tested, with inorganic species such as KCl, NaCl, KOH, NaOH, etc. These species are present in the syngas at about 800°C at the gasifier outlet and have to be eliminated to prevent as much as possible further interaction in heat exchangers. Aerosol sizes are between 0.1 and 100 µm. Tests were performed at 400°C and 800°C. The main problem to face when using such a filtration medium is plugging that can reveal, at elevated temperature, to be irreversible. This irreversibility may be caused by chemical reaction between the filtering medium material and the filtered particles. Main results of tests (not yet published) are the following:

- the metallic filtering medium (containing chromium) shows a small external layer of chromium oxide all around the grains and some precipitates containing K and Na in the peripheral zone;
- the ceramic filters grains are covered with a thin layer containing sodium, and some precipitates are also found in the matrix;
- for both media, due to the deposits, the pressure drop increased during the tests, up to the total plugging that occurred for different durations of the tests, depending on the material and the particle flow.

The filtering candles with another, larger, experimental device were also tested and showed the same tendencies, with larger deposits and larger reaction layers. Conclusion is that this filtration technique with metallic or ceramic industrial candles, that shows a filtration efficiency of more than 99%, will obviously lead to some irreversible plugging.

4.3.2 Electro-Filtration Results

Electro-filtration is a classic and efficient method for particles trapping at ambient temperature. At 800°C the electrofiltration is not so simple to implement. As part of the EPURGAS project, this technique was studied in a temperature range between 500 to 800°C. An experimental electrostatic precipitator (ESP) designed by LOCIE (*Université de Savoie*) was connected to the fluidized bed reactor of CEA and tests were performed with a real syngas produced from wood gasification (Villot *et al.*, 2012).

The filtration efficiency obtained was greater than 95% at 500°C. It has been shown that it is possible, above 500°C, to remove the particles contained in a syngas produced from biomass gasification. For higher temperature, electrical insulation problems occurred and some leakage of the current is noticed resulting in a decrease of the voltage. Tests performed at 680°C showed a variation of the potential difference between the electrodes due to particles deposition forming an electrical short-cut.

Taking into account technical improvements that can be made in the electrical insulation, the maximum temperature at which it seems possible to work with an ESP at an industrial scale is around 700°C.

4.3.3 Thermophoretic Filtration Results

Thermophoretic filtration is a way studied in the frame of the THERMOCAPT project. When a particle is submitted to a temperature gradient a thermophoresis force is applied to the particle and carries it to the cold wall. A thermophoretic filter was built and tested with model gas and real syngas. The main parameter is the temperature gradient; it has been adjusted at 60 000°C/m between two tubes separated by 5 mm. The cold tube was maintained at 300°C and the hot tube at 600°C. Particle deposition was observed only on the cold tube showing the reality of the thermophoresis effect. The filtration efficiency measured was very variable between 15 and 78% depending on numerous parameters (flow rate, temperature gradient not really homogeneous due to thermal exchanges with the syngas and walls of the filter, particle sizes, particle interactions, etc.). Interpretation

of the results is not easy and further studies are necessary to design an efficient and reliable thermophoretic filter. Nevertheless, it has been shown that such a filter could be useful for final filtration and high temperature for submicronic particles.

4.3.4 Conclusion

The different hot filtration devices tested showed that none of them is currently 100% satisfactory. Depending on the temperature and the particle size, some of the tested devices could be convenient: ceramic or metallic candles could be used up to about 600°C, with an increasing risk of non-reversible plugging at higher temperatures, ESP can work up to 700°C with improvements, thermophoretic filtration could be useful for final filtration and high temperature for submicronic particles.

4.4 Slag Formation and Interactions with Reactor Wall

An entrained flow reactor is a high temperature (~1 300°C to 1 500°C) chamber within which the conversion of the resource leads to a syngas mainly formed of CO, H₂, CO₂ and H₂O. The elevated temperature allows at the same time:

- the production of a CO and H₂ rich gas, also at elevated pressure (up to ~ 80 bar);
- methane reforming;
- tar reforming;
- ash meting.

The inner reactor wall is designed to resist to high temperatures in direct contact with liquid ash slag.

A known concept of interest for the inner wall is based on the use of solidified ash as refractory liner. This concept can be seen as a “cold crucible” or “self insulation” technique.

The wall is made of an external cooling system supporting a liner material formed of a thermally conductive ceramic, such as SiC (thickness ~ few centimetres). The reason for the high conductivity of the ceramic liner is a better distribution of the heat flux on the tubes of the cooling system. The ash solidifies on this liner and forms the thermal insulation layer. The temperature gradient is, thus, mainly located in the solidified ash layer. The high temperature liquid ash flows over the solidified ash layer. The principle of such a wall is shown in Figure 6.

This concept must comply with several constraints:

- heat losses should be limited (50 to 100 kW/m²);
- the thickness of the solidified ash should be limited (due to limited mechanical resistance of the wall support structure);

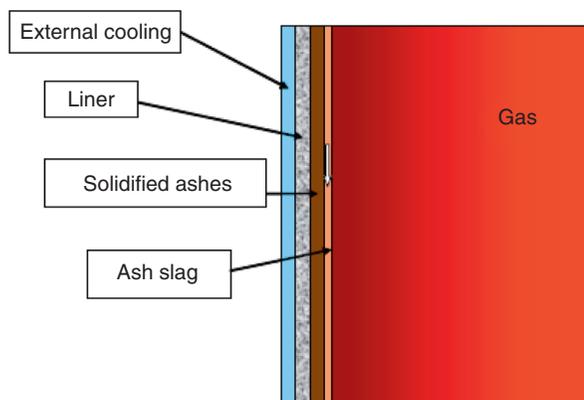


Figure 6
Schematic view of the “self insulated” wall.

- the wall should be able to withstand transient thermal loads;
- the investment cost should be reduced.

As the heat losses are mainly linked to conduction heat transfer through the solidified ash layer, these constraints lead to a typical thickness of centimetre for the solidified slag layer.

On the other hand, the heat flux is also imposed by heat transfer in the gas. In order to minimize the heat losses, the temperature difference between the gas temperature and the interface temperature with the liquid slag should be reduced. This interface temperature is linked to the melting characteristics of the slag.

If thick insulation ceramics are used instead of a solidified slag layer, the interface temperature is near to the gas temperature (which reduces the heat losses) but the ceramic material could dissolve into the molten slag, which leads to ceramic erosion and to the necessity to replace this ceramics regularly (induces maintenance costs). This kind of attack of a ceramic layer also depends on slag melting properties.

The melting properties of ash are therefore a key point for the operation of entrained flow reactor.

The important melting property that has been identified by many authors (Browning *et al.*, 1999) (Van der Drift *et al.*, 2004) is the viscosity of the slag. There is a tendency towards an agreement to limit the viscosity of the slag to 25 Pa.s in order to ensure a slag flow on the reactor wall. This viscosity is determined on the basis of existing models, like the model developed by Urbain and which has been originally developed for the calculation of the viscosity of lava (Seiler and Ganzhorn, 1997).

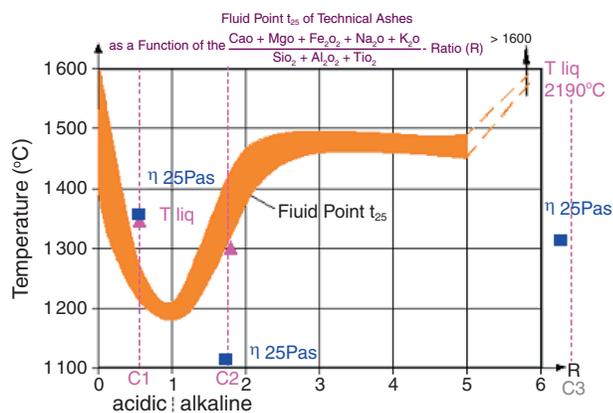


Figure 7

Link between EFR operation temperature and slag properties. The large line represents the result of industrial experience. The squares correspond to the operation temperature that is linked to a slag viscosity of 25 Pa.s and the triangles to the liquidus temperature derived from CEA analysis. It can be seen that the “thermodynamic temperature” approach is closest to the industrial experience.

4.4.1 CEA Approach

A different approach has been developed by CEA. This approach is based on the analysis of metallurgical and physico-chemical processes that take place on the interface between solidified ash and molten slag. This approach leads to the conclusion that the interface temperature tends towards the liquidus temperature that is in turn strictly linked to the ash composition.

Figure 7 presents a comparison of the different criteria used to determine the operation temperature as a function of slag composition (that is represented here by the ash composition ratio (R)). The large line represents the result of industrial experience. The squares correspond to the operation temperature that is linked to a slag viscosity of 25 Pa.s and the triangles to the liquidus temperature derived from CEA analysis. It can be seen that the “liquidus temperature” approach is closest to the industrial experience.

4.4.2. Conclusion

The CEA approach allows the elaboration of a deterministic methodology that enables:

- either, to determine the optimum reactor operation temperature as a function of the actual ash composition;
- or, to determine the composition and amount of additives that can be mixed with the resource in order to

reach a pre-determined operation temperature and slag viscosity for a given ash composition.

This technique allows therefore, adapting the operation parameters of an entrained flow reactor to diverse resources in order to control simultaneously:

- the thickness of the solidified ash layer;
- the slag viscosity;
- the heat losses.

Of course, reliable thermodynamic data bases are required for the calculations of the properties of slag mixtures. An effort to create and validate such data bases, and related methodologies, has been undertaken as part of the ANR INORGANIC and SLUGAS project.

For ceramic insulated reactors, the methodology also allows to determine, on the basis of ash composition, the optimal operation temperature that minimizes the ceramic ablation.

GENERAL CONCLUSION

The objective of this paper is to provide an up to date review about the behaviour of inorganic species in various processes. Focus was made on the work of the CEA, performed with different partners in the cited ANR projects.

Following topics were developed:

- inventory of inorganic species in different feedstock;
- general review of the inorganic speciation during thermal conversion processes: each species family has a specific behaviour, the most important data were reported;
- technological barriers to overcome for economic and technologic processes improvements: fluidized bed agglomeration, behaviour of the high temperature wall in an entrained flow reactor, corrosion of the heat exchangers and interactions with catalysts were pointed out in this paragraph;
- specific aspects related to inorganic species behaviour are or were investigated at CEA, a summary is given. Some more detailed results are reported on the 2 first issues:
 - inorganic species release and condensation;
 - aerosol behaviour and deposits;
 - hot particles filtration,
 - slag formation and interactions with reactor wall.

The issue about inorganic species and biomass is one of the current and important problems to improve the efficiency and cost of biomass thermal conversion facilities. Maintenance costs may quickly become important in case of high temperature processes due to the high corrosive potential and risk of fouling linked to these species.

In the future, as wood is going to be highly solicited for number of applications, prices will increase and other feedstock will be of interest (waste, sludge, etc.). As a consequence the difficulties linked to larger amounts of inorganic species (and may be other pollutants) will also increase! CEA and partners started studying such other feedstock: all these studies have to be continued to improve the understanding, to find new solutions in order to improve the competitiveness of all these processes.

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