Slag Formation and Corrosion of SiC-refractories in Biomass Gasification Reactors

L. Colombel, J. Poirier

During the gasification of biomass, inorganic species are produced and constitute an important obstacle in this process. Inorganics are the mineral elements and compounds present in biomass apart from the main gas (CO, H_2, CO_2, H_2O, CH_4) and organic species. They play an important role on the gas phase pollution and on the corrosion of the refractory structure. The objective of this study is the understanding of the corrosion of the refractory lining by the liquid ashes (slag).
The walls are externally cooled to reach a low temperature at the interface with the solid ash layer. The ashes condensate and solidify on the refractory wall. This ash layer plays the role of a thermal insulating lining to minimize the heat losses and to protect the refractory layer against all external attacks. The chosen material is a silicon carbide containing ramming paste to ensure the higher conductivity.
Lab tests show a limited corrosion of the SiC ramming paste. Oxidation of silicon carbide grains by iron oxide from liquid ashes is observed. The silica quantity is higher in the liquid ashes in contact with silicon carbide grains, which leads to an increase in liquid viscosity. The refractory wall is also protected by three effects:
• The highly viscous layer of ashes, which limits the slag penetration into the porosity of the ramming paste.
• The low temperature of the wall, which solidifies the liquid ashes.
• The no wettability of the carbon, which minimizes the slag/refractory lining interactions.

1 Introduction

In Europe it is very important to develop renewable energies in order to greatly reduce greenhouse gas emissions. Biomass is one of the most important renewable energy sources.

The use of biomass energy has the potential to increase fuel diversification and reduce dependence on foreign oil.

It can be gasified in entrained flux reactor to produce heat and electricity, or to synthesize biofuels (methanol, DME, *Fischer-Tropsch Diesels*) and high value molecules.

An entrained flow reactor is a high temperature (~1300 – 1500 °C) chamber within which the conversion of the biomass resource leads to a syngas mainly formed of CO, H_2, CO_2 and H_2O [1].

The elevated temperature permits to obtain a CO and H_2 rich gas, also at elevated pressure (up to ~ 80 bar). A typical biomass entrained flow reactor is showed in Fig. 1.

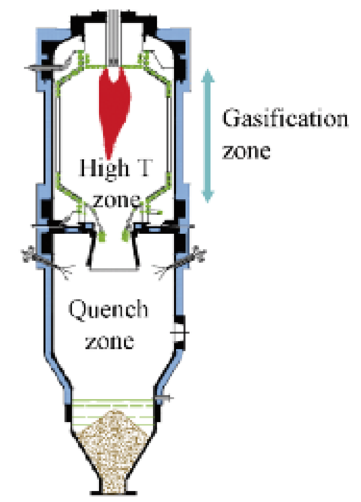

Fig. 1 Biomass entrained flow reactor

Inorganics are the mineral elements and compounds present in biomass apart from the main gas and organic species.

During gasification of biomass, some of the inorganic species form liquid or gas compounds and react with the refractories [2 – 4]. Consequently, the refractories are submitted to thermochemical stresses combined with a thermal gradient that limit their performance.

SiC refractory material is well adapted to the working conditions of gasification. However,

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Keywords: SiC refractories, biomass gasification, miscanthus ash, corrosion

Received: 29.01.2014
Accepted: 17.02.2014

the interactions of inorganic species with SiC refractory lining are not well understood. The objectives of this paper are a better understanding of degradation mechanisms [5] and the determination of main parameters governing SiC refractories wear in the biomass entrained flow reactors.

2 Interactions between slag and refractory lining

The gasification chamber of biomass is composed of SiC refractory lining covering metallic tubes in which high pressure water circulates (Fig. 2). Thanks to their high thermal conductivity, SiC refractories protect the metallic casing against high temperature corrosion and promote thermal transfer from flue-gas.

The wall is cooled externally to reach a low temperature at the interface: SiC refractory/solid ash layer. The ash solidifies on the SiC lining, forms a thermal insulation layer. This solid ash layer minimises heat losses and protect the SiC refractory lining against corrosion. The liquid slag flows over the solidified ash layer. It is the concept of the "cold crucible", based on the use of solidified ash as refractory liner.

The heat losses are mainly linked to conduction heat transfer through the solidified ash layer.

In steady state, the heat flux is constant and the interface temperature: liquid slag/solidified ashes is linked to the liquidus of the slag that depends on the composition of biomass ash. Thus the optimum reactor temperature that promotes the formation of a solid insulation layer can be determined as a function of the ash composition.

If the solidified slag layer is eroded, the SiC refractories is dissolved by the molten slag, which also depends on characteristics of biomass ash.

Therefore, the melting properties [6, 7] of biomass ashes (liquidus and solidus temperatures, the solid fraction in function of temperature and crystallization phases) are a key point for the working conditions of entrained flow reactor [8].

3 Melting properties of biomass ashes

The ashes of biomass are mainly composed of oxides (CaO, SiO_2, K_2O, MgO, Na_2O). Chloride and sulphur are minor elements. The composition of ashes depends on the origin of the biomass. Tab. 1 gives a typical composition of ashes close to miscanthus ash which is rich in SiO_2. The selection of this type of ashes is justified by the great potential of miscanthus for biomass valorization.

The liquidus temperature and the amount of solid and liquid phases have been calculated with the thermodynamic software Factsage [9].

Factsage© is a fully integrated database and software package developed jointly between *Thermfact/CRCT* (Montreal/CA) and *GTT-Technologies* (Aachen/DE). The associated databases for this study are: ELEM (elements thermodynamic database), FACT (gas species, solid and liquid compounds thermodynamic database), and FT oxid (compounds and solutions for oxides database). Fig. 3 shows the phases formed as a function of the temperature for the miscanthus ash composition.

The liquidus temperature of miscanthus ash is 1324 °C. The calculation predicts the formation of two immiscible liquid phases called slag 1, which is rich in SiO_2, and K_2O and slag 2, which is rich in SiO_2 and

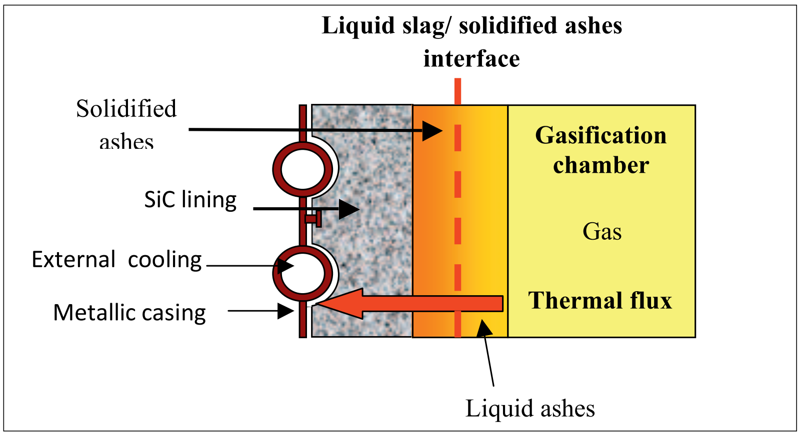


Fig. 2 Refractory structure composed of SiC lining and metallic casing

Tab. 1 Typical composition of miscanthus ash [mass-%]

Composition	Miscanthus Ash [mass-%]
SiO_2	60
Al_2O_3	5
Fe_2O_3	3
CaO	13
MgO	4
K_2O	14
Na_2O	1

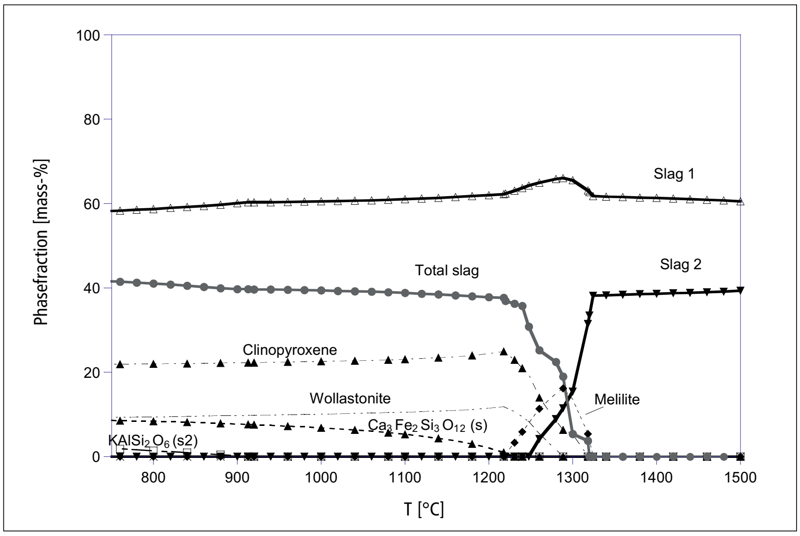


Fig. 3 Phases formed [mass-%] as a function of the temperature for miscanthus ashes

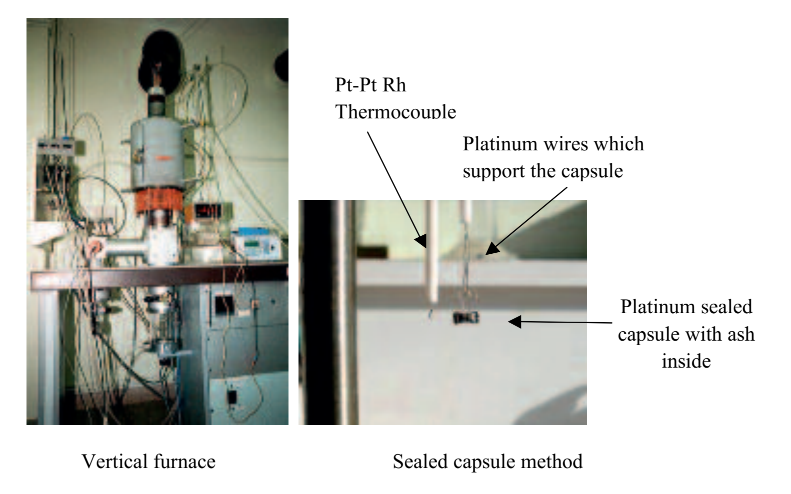


Fig. 4 Quenching furnace

Tab. 2 Liquidus temperature of miscanthus ash

Miscanthus Ash	Liquidus Temperature [°C]
Thermodynamic calculation	1324
Experimental result	1231

CaO. The primary crystallization phase is melilite.

The crystallization phases are composed of melilite ($Ca_2MgSi_2O_7$), clinopyroxene ($CaMgSi_2O_6$), wollastonite ($CaSiO_3$) and a silicate of alumina and potassium ($KAlSi_2O_6$).

An experimental approach has also been used to determine the liquidus temperature of miscanthus ash and to identify the phases crystallizing below the liquidus. Experiments were performed using a quenching method [10] in a sealed capsule to avoid the alkaline vaporization and by SEM observation, performed with a *F.E.I.* XL 40 TMP SEM.

Around 40 mg of miscanthus ash is prepared, enclosed in a sealed platinum capsule and inserted into the vertical furnace at a steady temperature for 3 h.

A thermocouple (Pt-Pt Rh 10 mass-%) is located close to the capsule to measure the temperature (Fig. 4). Quenching is obtained by applying a high voltage to the Pt wires. As a result, the capsule falls into the cold part of the furnace, allowing the melt phases to quench into a glass or a quench crystallized phase.

The temperature of liquidus is determined within a range of 5 °C. It is obtained by bracketing the disappearance of crystals by successive interactions at different quench temperatures.

Below the liquidus temperature, crystals in the shape of needles are observed. The number of crystals decreases as temperature rises while their size increases. The chemical analysis shows that crystals are wollastonite $CaSiO_3$. The glass quenched at 1234 °C does not contain any crystals (Fig. 5). The liquidus temperature is bracketed between 1228 – 1234 °C; it is around 1231 °C.

The experimental value of liquidus: 1231 °C is compared to those obtained by thermodynamic calculations (Tab. 2).

A 93 °C discrepancy between the measured and calculated liquidus temperatures of miscanthus ashes is observed. The primary crystallization phase predicted by thermodynamics, the melilite ($Ca_2MgSi_2O_7$) followed with clinopyroxene ($CaMgSi_2O_6$) and then wollastonite ($CaSiO_3$), is only in agreement with experimental results for the formation of the wollastonite. The two immiscible liquid phases predicted by the calculation are not observed.

Thus, if thermodynamic calculations need to be used to predict the liquidus temperature of typical ashes from biomass gasification for fuel production, it is necessary to improve the database where alkalis are present which clearly is indicated in the FACT document.

4 Corrosion of SiC refractories by liquid biomass ashes

Biomass gasification for fuel production in an entrained flow reactor is a technique in developmental stage. No industrial feedback is available so far.

Consequently, the corrosion resistance of SiC refractories by biomass liquid ashes has been studied in laboratory.

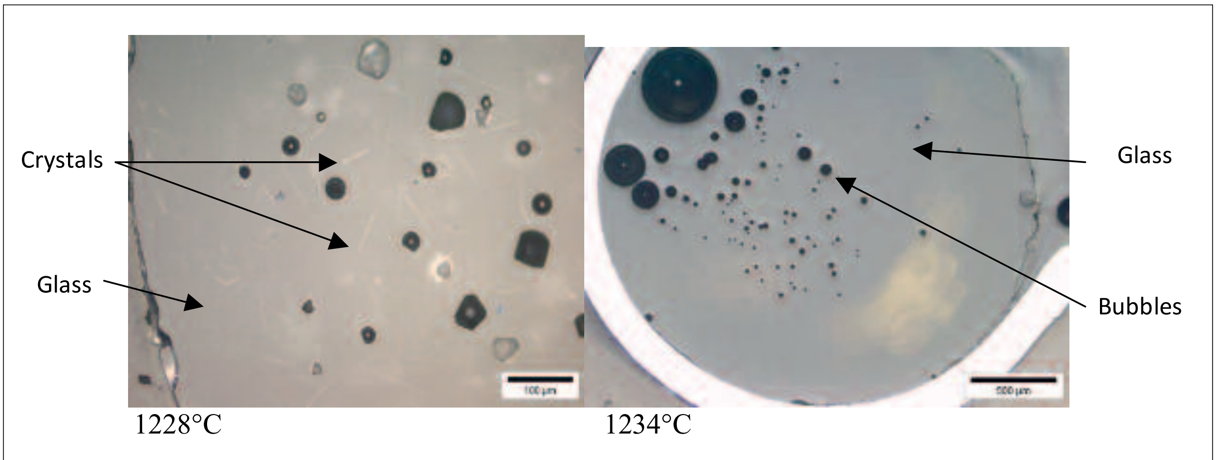


Fig. 5 Microstructure of miscanthus ash quenched at 1228 and 1234 °C respectively, with sealed capsule

Tab. 3 Characteristics of SiC ramming mass

Composition	[mass-%]	Physical Properties	
SiC	67	Bulk density	2250 kg/m³
C	19	Open porosity	20 %
Si	1	Thermal conductivity at 1000 °C	8,5 W/m · K
Clay	4		
Si_3N_4	2		
Others	2		

Tab. 4 Punctual EDS analysis at the corrosion interface (see Fig. 7)

[mass-%]	SiO_2	CaO	MgO	K_2O	Na_2O	Al_2O_3	Fe_2O_3
EDS analysis 1	70,7	8,1	3	11,3	0,9	6,1	–
EDS analysis 2	76,5	–	–	11,2	–	12,3	–
EDS analysis 3	75,2	–	–	11,6	–	13,2	–
EDS analysis 4	67,7	0,6	–	13,2	1	5	2,7

The use of silicon carbide ramming mass is a suitable choice because it is easy to apply. Tab. 3 gives the typical properties of this type of SiC ramming mass.

The ramming mass is made of SiC aggregates and a matrix composed of clay, graphite flakes and additives (Si, Si_3N_4).

Laboratory corrosion tests, using the static crucible method, were performed at 1300 °C for 5 h with miscanthus ash (see composition Tab. 1), in a reducing atmosphere, close to the real conditions.

Fig. 6 shows the corrosion apparatus. In practice, a double protective crucible of carbon is used around the SiC ramming mass crucible, in order to promote the formation of carbon monoxide at high temperature. This carbon crucible is placed in a high alumina dense refractory crucible to protect the carbon from oxidation by air in the electric furnace.

The corrosion is very weak. Liquid ash infiltrates into the matrix of the ramming mass and react with SiC fine particles (Fig. 7). The penetration of liquid ashes is limited by the carbon (graphite flakes and amorphous carbon), which is an excellent non-wetting agent, present in the matrix of the SiC ramming mass.

Around the SiC aggregates, a silica rich layer is formed (Fig. 8). The presence of cristobalite is very limited.

Close to the SiC ramming mass – liquid ashes interface, the punctual EDS analyses reveal an increase in the silica, alkaline and alumina content, a decrease in the lime and magnesia content and the quasi-disappearance of iron oxides initially present in miscanthus ashes (Tab. 1).

The formation of the silica-rich layer is probably due to the oxidation of SiC by iron oxides present in the miscanthus ash:

$$3SiC + 2FeO \rightarrow 2\ FeSi + SiO_2 + 3C$$

Iron silicide species are observed in the microstructure (Fig. 8).

The alkaline species diffuse quickly through the silica-rich layer, which explains the increase in K_2O amount. The diffusion of MgO and CaO is lower. The increase in Al_2O_3 is due to the dissolution of fine particles of alumina initially present in the matrix.

At high temperature (1300 °C), the viscosity of the silica-rich layer (800 00 Pa·s according to *Urbain's* model [11] is higher than the miscanthus liquid ashes. Consequently, the

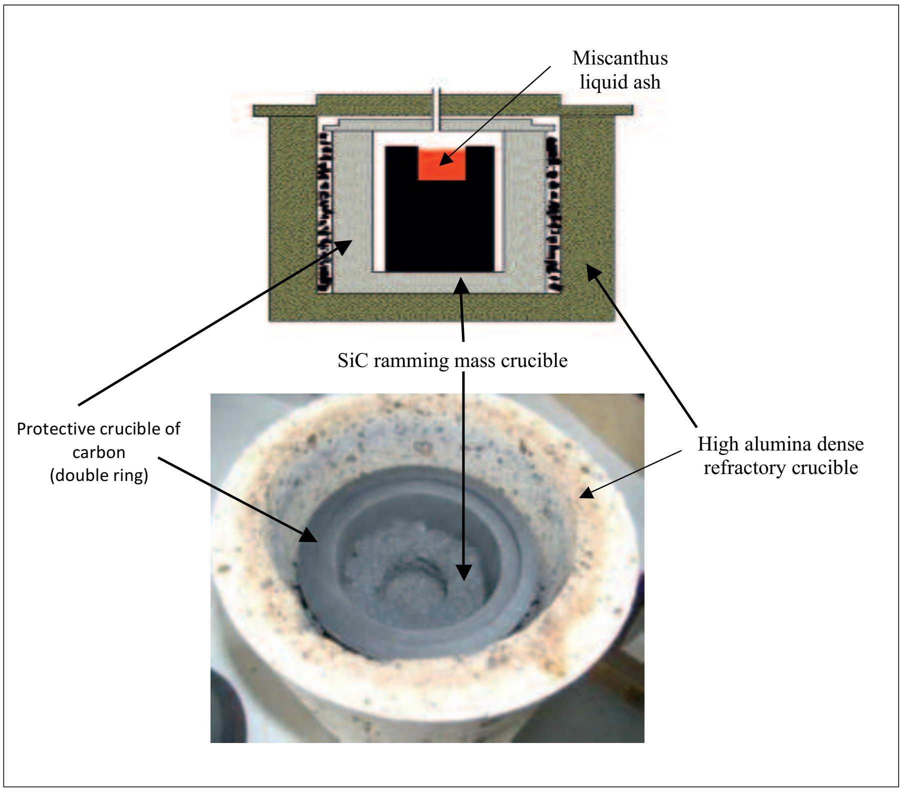
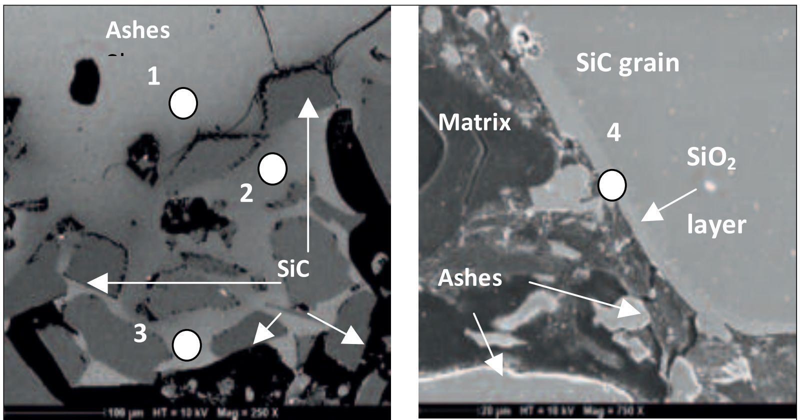


Fig. 6 Detail of the corrosion apparatus and view of the SiC ramming mass crucible



a) corrosion of the matrix

b) corrosion of a SiC grain

Fig. 7 Interface SiC ramming mass/ashes

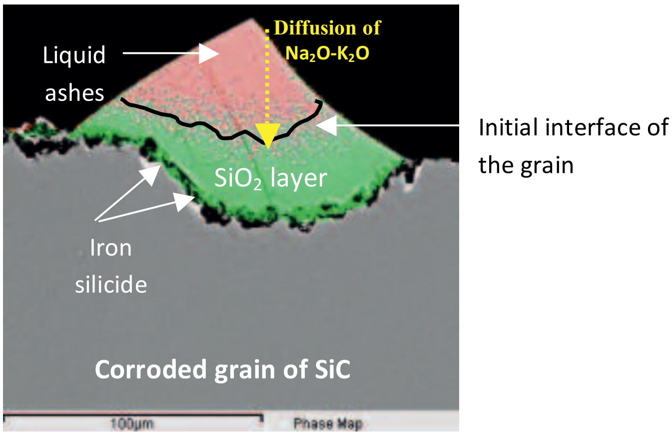


Fig. 8 Silica-reach layer at the interface SiC grain/liquid ashes

SiO_2 layer acts as a protective layer, limiting the diffusion of oxygen and the oxidation of silicon carbide.

5 Conclusion

The main objective of the publication is to provide a better understanding of SiC refractories wear in the biomass entrained flow reactors.

The role of the melting properties of biomass ashes (liquidus temperatures, the solid fraction in function of temperature) on the formation of a protective thermal insulation layer has been demonstrated.

The corrosion mechanism of a SiC ramming mass has been established:

- The slag penetrates into the refractory porosity.
- The alkaline species diffuse quickly through the silica-rich layer.
- Iron oxide present in the slag reacts with SiC aggregates to form new phases: iron silicide and a silica-rich layer SiO_2.

The SiO_2 layer acts as a protective layer, limiting the diffusion of oxygen and the oxidation of silicon carbide and the carbon of the SiC ramming mass limit the slag/refractory interactions.

Acknowledgments

This work was performed as part of the INORGANICS projects, partially funded by the French National Research Agency (ANR).

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