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Determination of the Liquidus Temperatures of Ashes from the Biomass Gazification for Fuel Production by Thermodynamical and Experimental Approaches

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During the gasification of biomass, inorganic species are produced and constitute an important obstacle in this process. The aim of this study is to understand the high temperature behavior of the inorganic species particularly the ashes close to the miscanthus and the straw ashes. A thermodynamic approach is used to obtain this characteristic. The database used for the calculation is first validated by comparison with systems available in the literature and by using an experimental approach. This study reveals the lack of optimization and the lack of data concerning alkali species and particularly K_2O-rich compositions. An experimental approach has been used to determine the liquidus temperature of ashes by a classical quenching method. Experiments using sealed capsules largely prevent the volatilization of K_2O. The liquidus temperature of three compositions with alkali and one without alkali were measured. A liquid miscibility gap is observed experimentally and by calculation for the straw ash.

1. Introduction

Biomass is one of the most important renewable energy sources. The use of biomass energy has the potential to greatly reduce greenhouse gas emissions. It is also a way to increase fuel diversification and reduce dependence on foreign oil.

The context of this research is the gasification of biomass for fuel production in an entrained flow reactor.[1]

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 and organic species. They play an important role on fluidized bed agglomeration, on the corrosion of the reactor wall, on the gas-phase pollution, or on the corrosion of the structure.

The overall objective of this work is understanding the behavior of inorganics under entrained-flow gasification conditions. Once gasification has taken place, the remaining solid, mainly ashes, will soften, liquefy and deposit on the walls, hereby forming the slag. A layer of solidified and molten ash will be condensed on a refractory wall. This wall is cooled externally. This ash layer will play the role of a thermal insulating lining to minimize the heat losses and to protect the refractory layer against external attacks.[2] The slag has to be liquid to be able to run down the wall.

This paper presents the results of the characterization of slag behavior, particularly the liquidus temperature. The study will be carried out for two typical compositions of ashes (Table 1).

The first one, which is rich in SiO_2 (C1), is close to the miscanthus ash, and the second one, with the same amount of SiO_2 and CaO (C2), is close to the straw ash contents. Apart from CaO and SiO_2, K_2O is an important component of the ash. The selection of these two types of ashes is justified by the great potential of miscanthus and straw for biomass valorization.

In the first part of this paper, the thermodynamic approach is described. The thermodynamic tool used is described and is validated by comparison with existing data from the literature. The liquidus temperatures calculated for the two typical ashes are then presented.

Second the experimental approach is described. The results for the ternary system ($SiO_2-CaO-K_2O$) and for the two typical compositions (C1 and C2) are presented. Finally, the thermodynamic and experimental approaches are compared.

The same kind of research combining experimental and thermodynamic modeling studies has already been successfully done on coal combustion slag.[3]

2. Thermodynamic Approach

2.1. Description of the Thermodynamic Calculations. The calculation is based on the minimization of the Gibbs energy of the system. It is thus possible to deduce the nature of the solid, liquid and gaseous phases as well as their chemical compositions at the thermodynamic equilibrium. This knowledge makes it possible to deduce the liquidus and solidus temperatures and the amount of the solid and liquid phases.

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Table 1. Typical Composition of Ashes

	C1 (wt. %)	C2 (wt. %)
SiO_2	60	34
Al_2O_3	5	1
Fe_2O_3	3	5
CaO	13	34
MgO	4	3
K_2O	14	22
Na_2O	1	1
total	100	100

Calculations have been carried out with Factsage (version 5.4.1).

Factsage is a fully integrated database and software package developed jointly between Thermfact/CRCT (Montreal) and GTT-Technologies (Aachen). It consists of a series of modules that access and manipulate thermodynamic databases and perform various calculations. Factsage is composed of two types of thermo chemical databases: compounds (i.e., pure substances, over 4,400 compounds) and real solutions.

- Compound databases are mainly for stoichiometric solid, liquid and gaseous species. Allotropes (for example cristobalite, tridymite) are included. Nonstoichiometric compounds such as FeO_x ($x = 0.947$) are also stored.
- Solution data are for solid and liquid alloys, ceramics, salts, mattes, slags, etc. The data are stored in the form of Gibbs energy functions for the phase constituents and parameters for the excess Gibbs energy of mixing between the phase constituents. Factsage supports several different solution models including simple polynomial models such as the Redlich−Kister or the Legendre polynomial combined with different higher order extrapolations (Muggianu, Kohler, Toop), the quasichemical model, Pitzer parameters, and sublattice models.[4]

The associated databases for this study are: ELEM (elements thermodynamic database), FACT 53 (gas species, solid and liquid compounds thermodynamic database), and FT oxid (compounds and solutions for oxides database).

The expected equilibrium phases were predicted by using the "Equilibrium" module of Factsage considering as possible phases: the slag, several solid-solution phases and all liquid and solid compounds between the inputs. Oxide compositions are entered as initial compositions in weight percent in the submenu "reactants" of "Equilib".

The FToxid database contains data for pure oxides and oxide solutions of 20 elements. All the binary and ternary subsystems have not been evaluated and optimized, nor are all composition ranges covered. Subsystems which have not been evaluated and optimized have been assumed ideal or have been approximated.

Thus, this database contains the following major oxides: Al_2O_3, CaO, Fe_2O_3, MgO, SiO_2, and all the binary and many ternary and quaternary subsystems more or less optimized. Interaction between these five oxides should be correctly calculated.

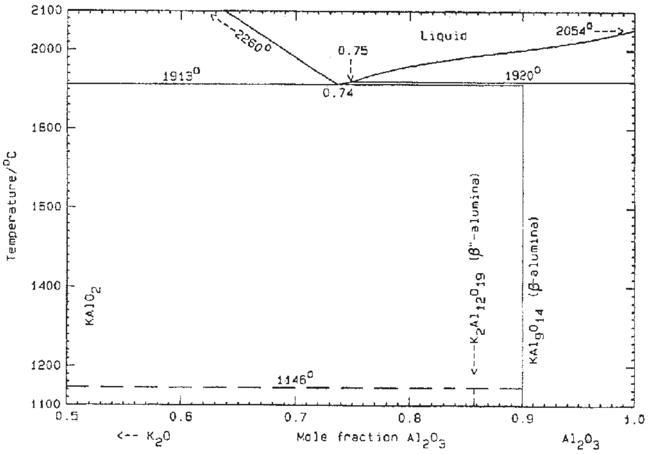

Figure 1. Binary diagram $K_2O-Al_2O_3$ [4].

Table 2. Liquidus Temperatures for C1 and C2 with and without Na_2O and K_2O

	C1 rich in silica (miscanthus)	C2 rich in K_2O (straw)
	with Na_2O K_2O	
$T_{liquidus}$	1324 °C	1256 °C
	without Na_2O K_2O	
$T_{liquidus}$	1560 °C	1420 °C

When Na_2O and K_2O are present, the Factsage documentation specifies that optimization is less accurate. Major improvements are in progress for these oxides.[5,6]

To conclude, the use of the thermodynamic FToxid database for the calculation of the liquidus temperature for the two compositions will be marred by some uncertainties due to the alkalis.

To ensure the reliability and the pertinence of the calculations, it seems necessary to validate the thermodynamic calculations for simpler systems with fewer oxides than the multi component ashes. Consequently, the main subsystems (binary and ternary) have been tested.

2.2. Validation of the Thermodynamic Calculations. The thermodynamic database FToxid is constructed from the optimization of several binary and ternary systems. A phase diagram is said to be optimized when all the data from the literature have been analyzed, evaluated, selected, and used to determine the main parameters to carry out the modeling of the phase diagram. The modeling is not always carried out for the complete compositional range of a system. To validate the FToxid database, calculations have been done in the most pertinent binary, ternary and quaternary systems.

To assess the validation of the FToxid database, the systems have been checked in two ways:

- For the optimized diagrams, the optimization has been checked in the studied domain of ashes C1 and C2. If the range of composition is not optimized, bibliographic research is done to check the existence of other measurements and to reproduce them by calculation from the database.
- For the nonoptimized diagram, bibliographic research is performed to find experimental results that are compared

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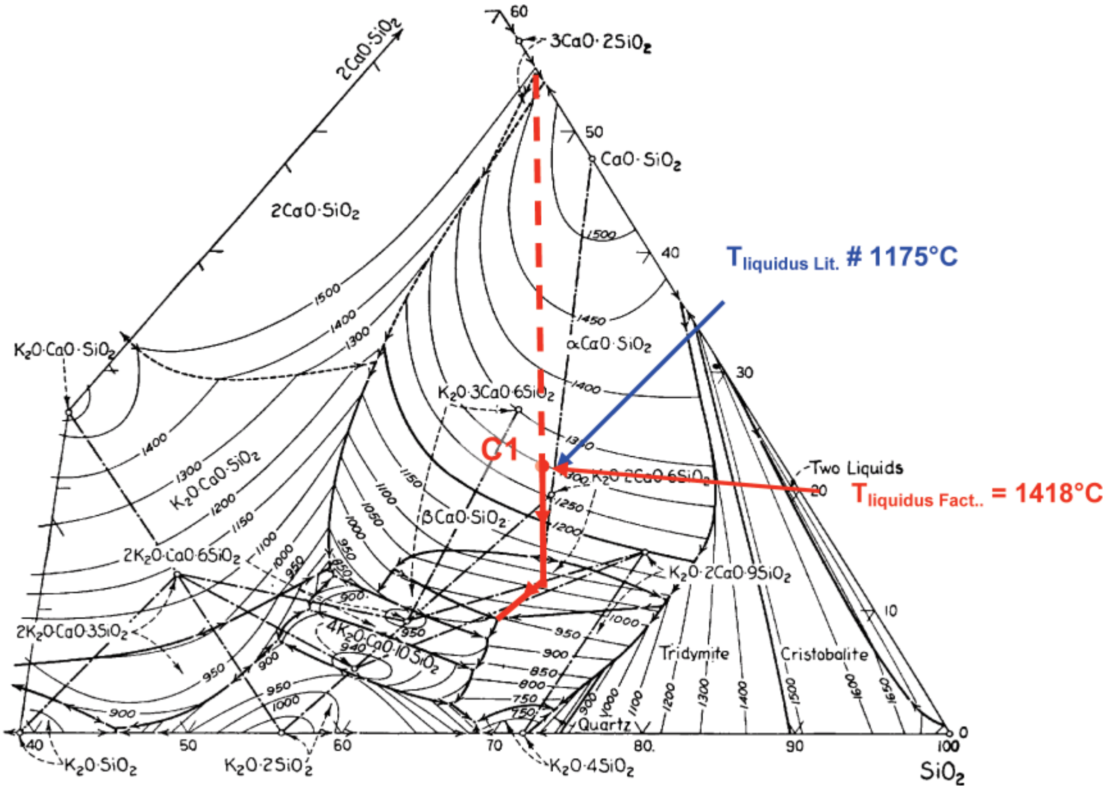

Figure 2. Ternary diagram $SiO_2-CaO-K_2O$ [13].

with the calculation. This comparison gives information about the validation of the database.

For the four main oxides SiO_2, CaO, Al_2O_3 and MgO, all the binary systems have been checked with the same proportions as the two ashes.[7−12] This has not been done for minor oxides such as Fe_2O_3 and Na_2O.

For K_2O, which is also a major oxide, K_2O-SiO_2 is the only optimized binary system.[13] It has been successfully checked for the two ashes compositions C1 and C2. The two other main binary systems K_2O-CaO and K_2O-MgO are not optimized in the FToxid database. Experimental data have not been found in the literature. It makes the validation of the database in this domain impossible.

On the other hand, $K_2O-Al_2O_3$ is optimized[7] but not in the composition range relative to ashes C1 and C2 (Figure 1). Besides, experimental data has not been encountered in the literature to validate the database in this domain.

Concerning the ternary systems resulting from the major oxides SiO_2, CaO, K_2O, MgO, only $SiO_2-CaO-MgO$ is optimized[14] and successfully checked for the two ashes C1 and C2. This result is in agreement with the literature.[15,16] No data has been published for $CaO-K_2O-MgO$ system. Experimental data has been encountered in the literature for SiO_2-K_2O-MgO[17] and $SiO_2-CaO-K_2O$.[18] Validation of the database has been poorly obtained for these two ternary systems. Particularly the liquidus temperature is higher 200−400 °C for C1 and C2 as illustrated, for example, for C1 in $SiO_2-CaO-K_2O$ (figure 2).

2.3. Calculation Results for the Typical Ashes. The liquidus temperatures calculated with Factsage are presented in Table 2 for the two ash compositions with and without Na_2O and K_2O.

2.3.1. Composition C1. Without Na_2O and K_2O, the liquidus temperature is 1560 °C (Figure 3). The primary crystallization phase is SiO_2. With Na_2O and K_2O, the liquidus temperature (1324 °C) is lower by around 230 °C

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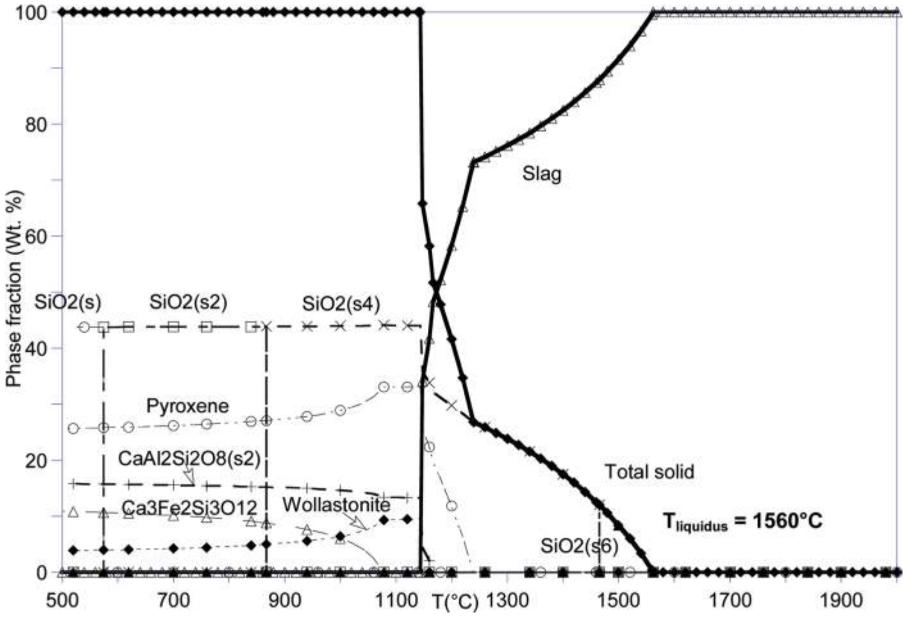

Figure 3. Weight percent of the phases formed as a function of the temperature for C1 without Na_2O and K_2O.

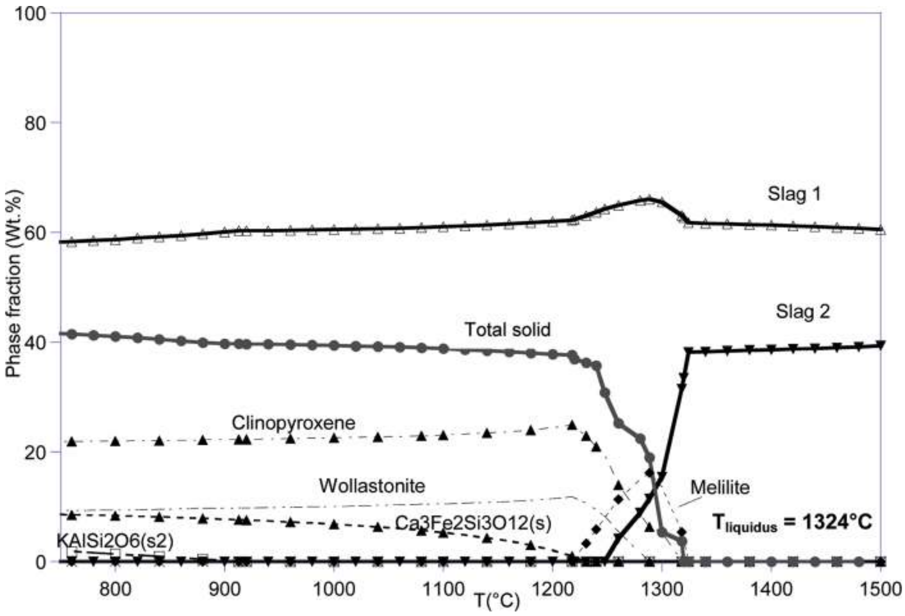

Figure 4. Weight percent of the phases formed as a function of the temperature for C1 with Na_2O and K_2O.

in agreement with the existence of a eutectic in the binary system with silica (Figure 4). 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 CaO. The crystallization phases are composed of melilite ($Ca_2MgSi_2O_7$), clinopyroxene ($CaMgSi_2O_6$), and wollastonite ($CaSiO_3$).

2.3.2. Composition C2. Without Na_2O and K_2O, the liquidus temperature is 1420 °C (Figure 5).

The primary crystallization phase is wollastonite. With Na_2O and K_2O, the liquidus temperature (1256 °C) is lower by about 170 °C (Figure 6). The calculation predicts the presence of two immiscible liquid phases called slag 1, which is rich in SiO_2, and CaO and slag 2, which is rich in SiO_2 and K_2O. The primary crystallization phase is a spinel phase close to Fe_3O_4 in composition.

For both compositions, the modeling of Na_2O and K_2O with CaO, which is a major oxide, has not been optimized. Thus the liquidus temperature is quite uncertain.

Besides it is important to remember that ternary systems with K_2O ($SiO_2-CaO-K_2O$ and $SiO_2-MgO-K_2O$) are poorly validated by Factsage. The calculations are probably less reliable because of the lack of optimization for this oxide and both liquidus temperatures from calculation are probably too high.

To test the validity of these results it is necessary to compare them with experimental measurements.

3. Experimental Approach

3.1. Experimental Procedure. Experiments have been carried out in a vertical quench furnace at ISTO (Institut des Sciences de la Terre; CNRS laboratory, Orléans, France) (Figure 7). The

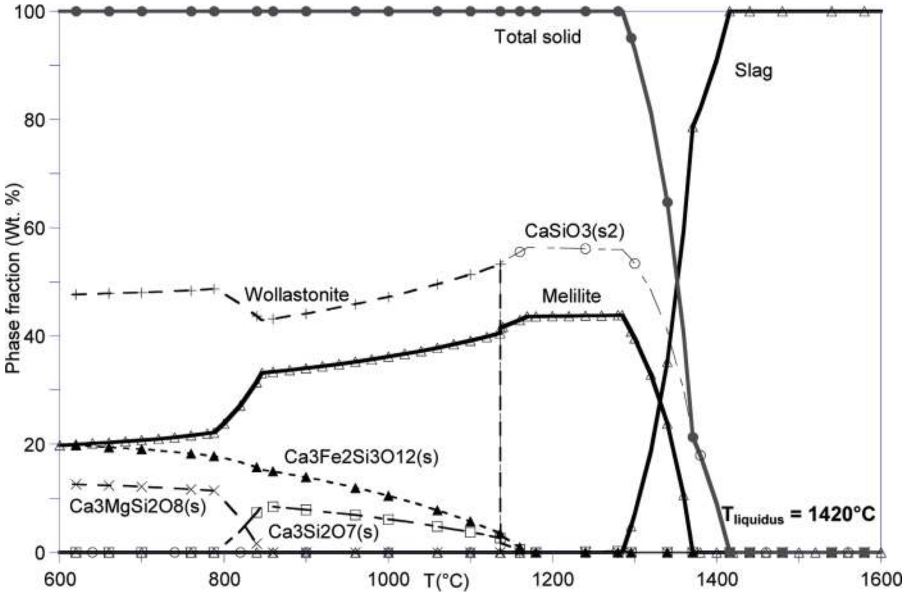

Figure 5. Weight percent of the phases formed as a function of the temperature for C2 without Na_2O and K_2O.

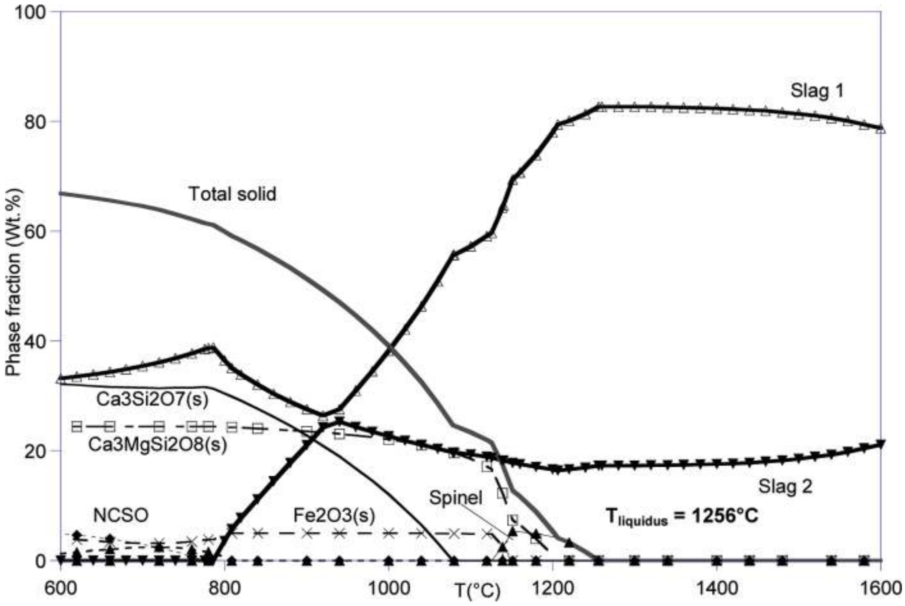

Figure 6. Weight percent of the phases formed as a function of the temperature for C2 with Na_2O and K_2O.

objectives of the experiments are to determine an experimental liquidus temperature and to identify the phases crystallizing below the liquidus. Experiments were performed using the quenching method.[19]

The starting sample is made of ground glass mixed with polyvinyl alcohol to ensure its cohesion during the installation in the furnace and which is later vaporised at low temperature. Two different procedures were used: one in an open system and the second one in sealed capsules. In the first one, an open system, the slurry obtained is then spread over a platinum hook (Ø = 0.2 mm) hung on a wider platinum wire (Ø = 0.5 mm) inserted into an alumina rod. A thermocouple (Pt−Pt Rh 10 wt.%) inserted into another alumina rod is located close to the sample to measure the temperature. For the second one, sealed capsules, the samples have been enclosed in sealed capsules to minimize the volatilization of the alkali oxides (K_2O and Na_2O) during the experiment.[20] Around 40 mg of powder is prepared. Capsules are made from a platinum tube of 2 mm in diameter and 10 mm in length. These capsules are cleaned, dried, and then arc welded (Figure 8).

For both procedures, the temperature distribution is uniform.

Daily fluctuation is less than to 2 °C and temperature is known to better than ± 5 °C. The whole assembly is inserted into a vertical furnace at a steady temperature for 3 h, under air.

Quenching is obtained by applying a high voltage to the platinum wires. This fuses the thinner wires (Ø = 0.2 mm). As a result, the sample falls into the cold part of the furnace, allowing the melt phases to quench into a glass or a metastable quench crystallized phase.

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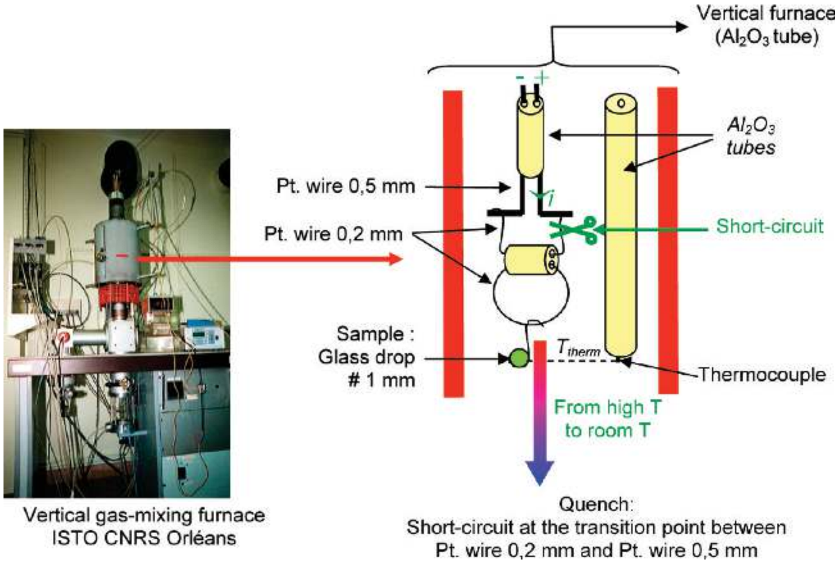


Figure 7. Quenching method.

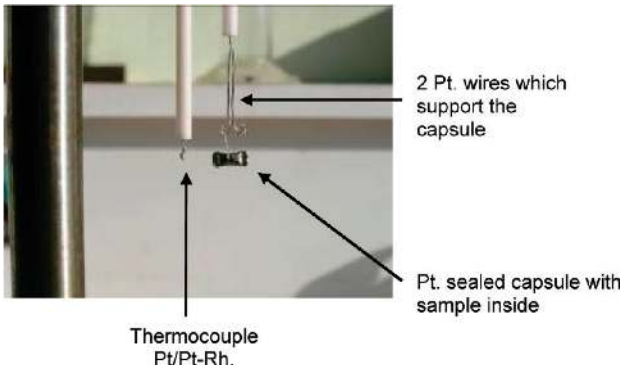


Figure 8. Sealed capsule method.

Once the sample has been quenched, the capsule is opened (if sealed capsule procedure). The glass is extracted and then polished for SEM (scanning electron microscopy) observations. WDS (wavelength dispersive spectroscopy) electron microprobe analysis is used for the determination of the composition of the experimental products.

The possible formation of crystals indicates if the sample was completely liquid at the temperature of the experiment. The liquidus temperature is obtained by bracketing the disappearance of crystals by means of experiments at different temperatures.

The experimental approach has been first validated with the ternary system $K_2O-CaO-SiO_2$. Second this approach has been applied to both ash compositions (C1 and C2).

3.2. Validation of the Method with the Ternary System $K_2O-CaO-SiO_2$. To validate this method, one composition called KCS was studied in the ternary system K_2O-CaO-SiO_2, in oxide proportion similar to the C1 composition (Table 3).

This ternary diagram has not been optimized in the FToxid database. However experimental data exist in the literature.[18] For this composition, the liquidus temperature, calculated with Factsage, is 1418 °C (Figure 4). It is higher than the one measured in the publication,[18] which is around 1175 °C.

The ternary composition has been prepared with K_2CO_3, $CaCO_3$, and SiO_2 oxides. Before the experiments, the powder was previously decarbonated by step heating at 700 and 900 °C. At the end of the experiment, a hollow ball with a diameter of about one millimeter is obtained, then polished and observed with SEM.

Table 3. Studied Composition in the $K_2O-CaO-SiO_2$ System

	ternary composition (% wt.)	composition C1 (% wt.)
SiO_2	69	60
CaO	15	13
K_2O	16	14
Al_2O_3	0	5
Fe_2O_3	0	3
MgO	0	4
Na_2O	0	1

The cross section of a glass ball, quenched at 1175 °C, reveals a ring of glass in which crystals, with a size of about 4 μm, occur (Figure 9).

For samples quenched between 1177 and 1225 °C, crystals are present for this specific composition. The crystals grow in size as the temperature increases, while their number decreases (Figure 10). At 1230 °C, no crystals are observed. The liquidus temperature is bracketed between 1225 and 1230 °C. The experimental temperature is close to the literature value[18] and differs from the calculated value (Figure 2). This result confirms the inability of the FToxid database to reproduce phase equilibria involving K_2O.

The chemical analysis reveals that the crystals are wollastonite ($CaSiO_3$), in agreement with the literature and the thermodynamic results.

3.3. Composition C1. This composition has been measured by the two procedures (open system and sealed capsule)

3.3.1. without the Sealed Capsule (*Open System*). This composition has been prepared by Schott (Table 4). The experimental composition (analyzed by electron microprobe) is in agreement with the miscanthus ash C1.

An iterative approach has allowed estimation of the liquidus temperature within a range of 5 °C.

Below the liquidus temperature, crystals in the shape of needles are observed (Figure 11).

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 1240 °C does not contain any crystals. The liquidus temperature is therefore bracketed between 1235 and 1240 °C.

The evolution of crystal and glass phases is followed with the electron microprobe as a function of the temperature. Data were obtained using a microscope image acquisition and analysis software package (Table 5).

The amount of crystal decreases as the temperatures rises, consistent with a closer approach to the liquidus temperature.

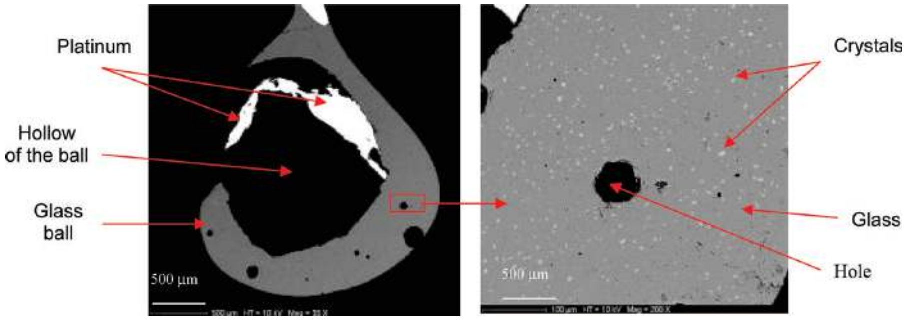
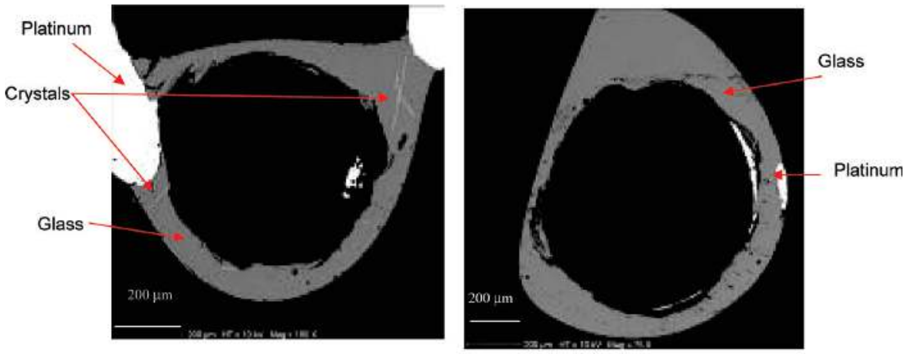


Figure 9. Glass balls quenched at 1175 °C for the ternary composition.



1225 °C

1230°C

Figure 10. Glass balls quenched at 1225 and 1230 °C for the ternary composition.

Table 4. Theoretical and Experimental Compositions of C1

	composition C1 siliceous slag close to miscanthus ash (% wt)	composition C1 given by Schott and analyzed (% wt)
SiO_2	60	61.3
Al_2O_3	5	4.9
Fe_2O_3	3	2.6
CaO	13	12.8
MgO	4	3.9
K_2O	14	13.5
Na_2O	1	1.1

This analysis shows the volatilisation of K_2O with increasing temperature (Table 5 and Figure 12). Up to 1240 °C, the volatilization of K_2O is weak. At 1240 °C, 1% wt. of the glass is volatilized which represents a loss of 10% wt. of the K_2O charge. Even if the experiment could be improved to avoid volatilization, this measure gives a good estimate of the liquidus temperature.

3.3.2. with Sealed Capsule. As in the former experiment without the sealed capsule, an iterative approach, by means of several experiments at different temperatures, has made it possible to estimate the liquidus temperature within a range of 5 °C. The liquidus temperature is around 1230 °C (Figure 13).

The evolution of crystal and glass phases is followed with the electron microprobe as a function of the temperature (Table 6) and K_2O is reported on the same graph as the experiments without capsules (Figure 12). The loss of K_2O is less important with the use of sealed capsule (less than 0.5 wt. % of the total K_2O).

In both cases, the loss of K_2O is quite weak. The liquidus temperature is confirmed and is around 1230 °C. This value is one hundred degrees lower than the thermodynamic calculation for alkali species which is 1324 °C (table 2). The composition of the liquid phase at the liquidus temperature is presented in table 7.

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. In addition, the presence of two immiscible liquid phases predicted by the calculation is not observed.

Table 5. Evolution of the Amount of Glass and Crystal As a Function of the Temperature Composition C1 without the Sealed Capsule (Open System)

	1170 °C	1216 °C	1235 °C	1240 °C	1278 °C
% wt. glass	89.1	96.7	99.8	100	100
% wt. crystal	10.9	3.3	0.2	0	0
% wt. K_2O (glass + crystal)	13	11.75	12.2	11.8	9.6

3.4. Composition C2. The composition C2 has been prepared by Schott (Table 8). This composition has been measured by the two procedures (open system and sealed capsule)

3.4.1. without Sealed Capsules (*Open System*). The composition C2 is richer poorer in SiO_2 and richer in K_2O and CaO. In this range of temperature and without a capsule, the experiments have shown significant vaporisation of K_2O at a temperature bellow 1280 °C. For the real composition, that is, without alkali species, as total K_2O vaporization has occurred, the liquidus temperature has been measured around 1375 °C (Figure 14).

This value is in reasonable agreement with the liquidus temperature predicted from the calculation without alkali species: 1420 °C (Table 2) and the primary crystallization phase is wollastonite $CaSiO_3$ (Figure 3). The evolution of crystal and glass phases is presented in Table 9.

3.4.2. with Sealed Capsules. At 1202 °C and at 1230 °C, two immiscible liquid phases are present together with a crystal phase From 1230 °C, the two immiscible liquid phases remain, but the crystal phase is no longer observed (Figure 15). A mass balance, performed by microprobe analyses, shows that the quench crystallized phases observed on the figure 15 have been formed upon quenching of the melt which makes the determination of the liquidus temperature less straightforward.

The compositions of these two immiscible liquid phases and the crystal phase are presented in Table 10 and Figure 16 ($K_2O-CaO-SiO_2$ ternary diagram).

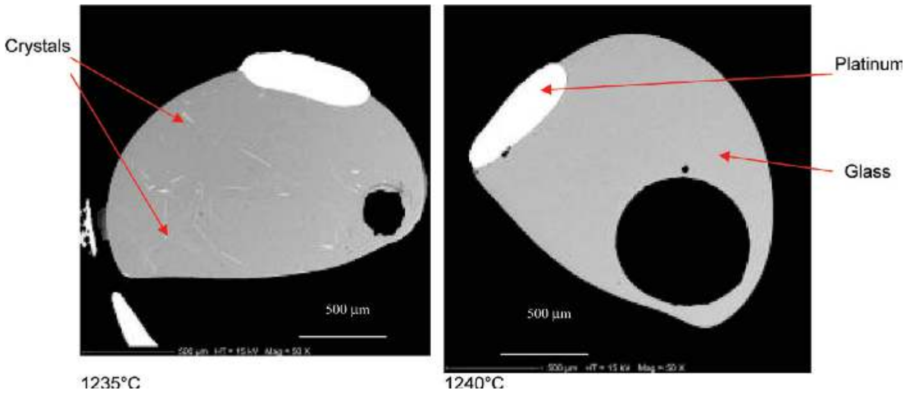


Figure 11. Glass balls quenched at 1235 and 1240 °C for composition C1 without sealed capsule.

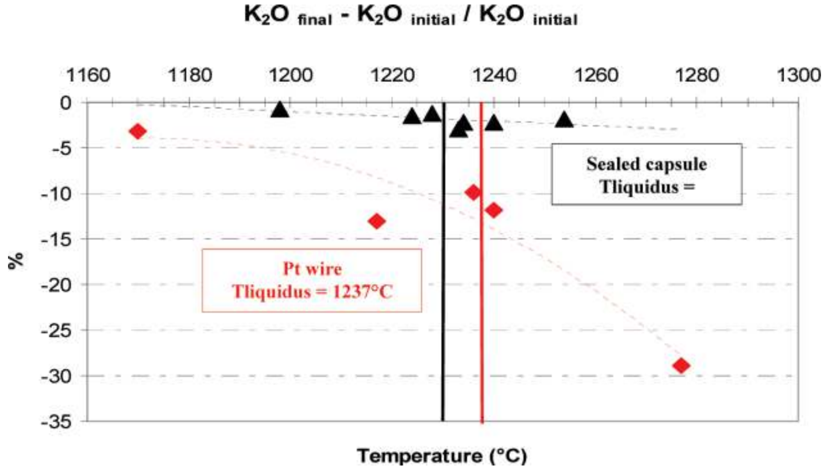


Figure 12. Evolution of K_2O with and without capsule as a function of the temperature in comparison with the initial composition C1.

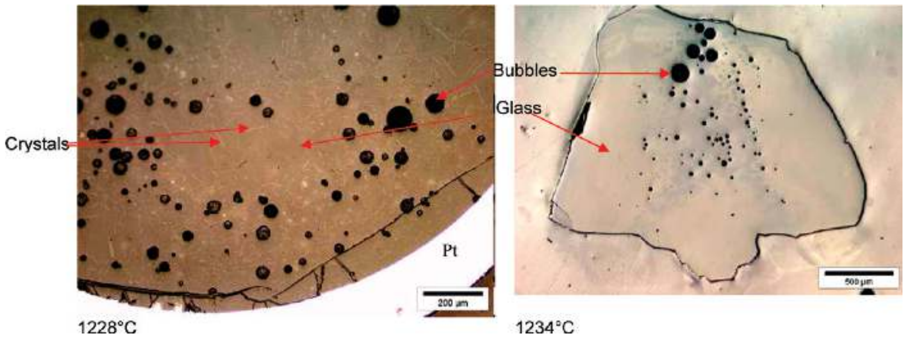


Figure 13. Glass balls quenched at 1228 and 1234 °C for composition C1 with sealed capsule.

Table 6. Evolution of the Amount of Glass and Crystal As a Function of the Temperature Composition C1 with the Sealed Capsule

	1198 °C	1224 °C	1228 °C	1233 °C	1234 °C	1240 °C	1254 °C
% wt. glass	90.9	95.9	97.0	100	100	100	100
% wt. crystal	9.1	4.1	3	0	0	0	0
% wt. K_2O (glass + crystal)	13.41	13.31	13.38	13.29	13.36	13.29	13.31

Table 7. Composition of Glass at the Liquidus Temperature (Experimental Values)

	K_2O	SiO_2	FeO	CaO	Na_2O	Al_2O_3	MgO
% wt.	13.29	61.63	2.47	12.71	1.02	4.92	3.96

Figure 17 shows the evolution of the ratio $K_2O/K_2O + CaO$ of the three phases between 1200 and 1400 °C. The melting temperature ranges between 1230 and 1295 °C.

This result is confirmed by DSC (differential scanning calorimetry; Figure 18). These results are in agreement

Table 8. Theoretical and Experimental Compositions of C2

	composition C2 close to straw ash (% weight)	composition C2 given by Schott and analyzed (% weight)
SiO_2	34	34.8
Al_2O_3	1	1.7
Fe_2O_3	5	4.3
CaO	34	33.2
MgO	3	5.1
K_2O	22	20.3
Na_2O	1	0.6

with the thermodynamic calculations which predict that this temperature is 1256 °C with the disappearance of the solid phase.

Table 9. Evolution of the Amount of Glass and Crystal As a Function of the Temperature Composition C2 without the Sealed Capsule (Open System)

	1296 °C	1316 °C	1348 °C	1357 °C	1362 °C	1372 °C	1376 °C
% wt. glass	66.7	72.5	77.5	82.5	84.1	87.8	100
% wt. crystal	33.3	27.5	22.5	17.5	15.9	12.8	0

4. Discussion

Measurements and calculations of liquidus temperatures of two typical ashes from biomass gasification for fuel production has been compared in this publication and are summarized in Table 11.

The liquidus temperature has been calculated with the thermodynamic software Factsage for two typical ash compositions. To assess the reliability of this calculation a validation step has been used. It reveals the reliability of the database concerning the studied system without alkalis. This excellent

Table 10. Composition of the Two Immiscible Liquid Phases and the Solid Phase C2 with Sealed Capsules

temperature		K_2O (% wt.)	SiO_2 (% wt.)	FeO (% wt.)	CaO (% wt.)	Na_2O (% wt.)	Al_2O_3 (% wt.)	MgO (% wt.)
1230 °C	liquid phase 1	4.5	34.2	0.4	57.9	0.3	0.04	0.9
	liquid phase 2	40.9	30.9	7.7	1.4	0.7	4.4	12.9
	solid phase 3	24.7	37.4	7.4	19	1	1.3	3.7
1295 °C	liquid phase 1	3.9	34.4	0.35	58.4	0.2	0.03	1.05
	liquid phase 3	25.4	36.9	6.93	19.3	1.1	1.5	4.5

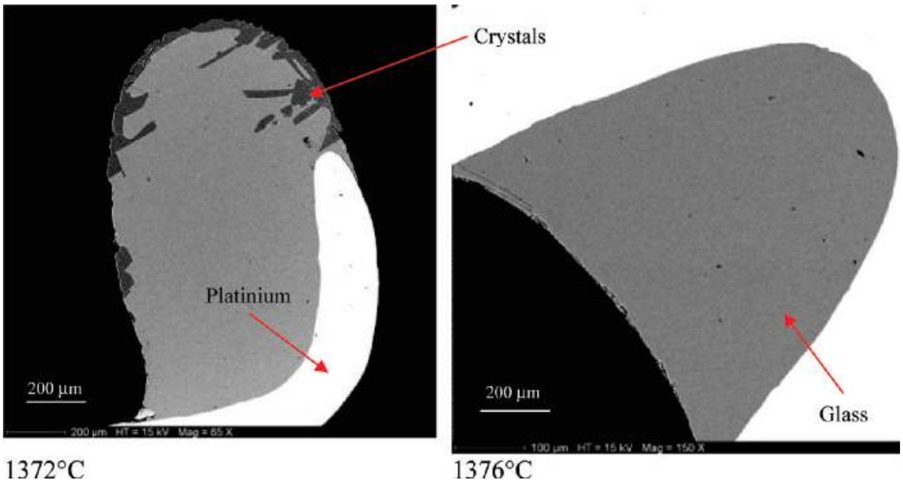


Figure 14. Glass balls quenched at 1372 and 1376 °C for composition C2 without sealed capsule.

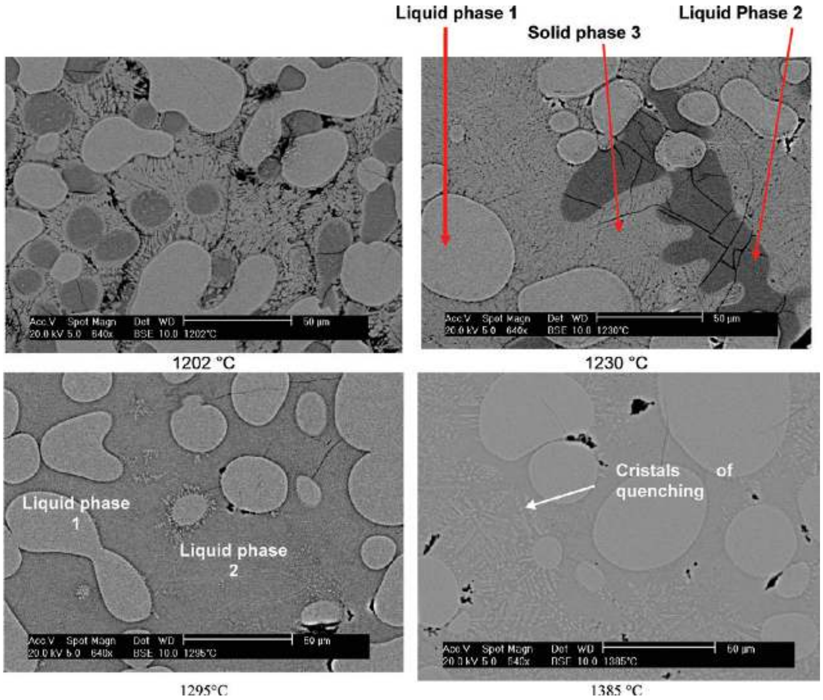


Figure 15. Glass balls quenched between 1202 and 1385 °C for composition C2 with sealed capsule.

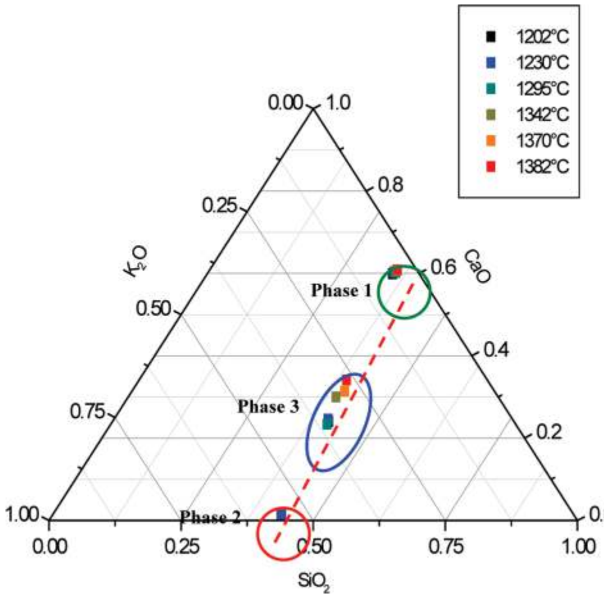


Figure 16. Composition (% wt.) of the phases 1, 2, and 3 ($K_2O-CaO-SiO_2$ ternary diagram).

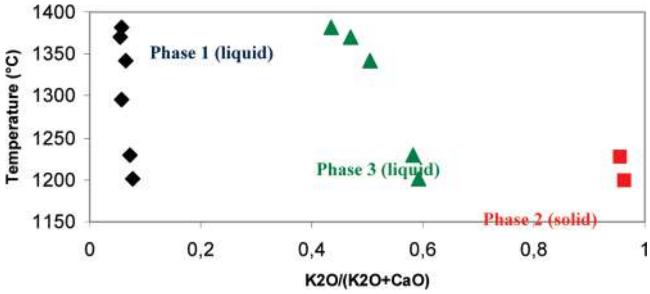


Figure 17. Compositions of three phases in a $K_2O-CaO-SiO_2$ ternary diagram.

agreement between F*A*C*T equilibrium calculations and measurements has already observed by Jack.[15,16] However, with alkalis, there is a lack of thermodynamic data and the database is very uncertain, which clearly is indicated in the F*A*C*T instructions. Indeed, with K_2O, only one binary system K_2O-SiO_2[13] is optimized. For the ternary system resulting from the major oxides with K_2O, no optimization is performed in the database, but measurements are published in the literature for SiO_2-K_2O-MgO[17] and SiO_2-K_2O-MgO.[18] For the others, the comparison with the literature exhibits strong differences which reveal the limitations of the FToxid database. Thus, the liquidus temperatures obtained from the calculation are not quite certain. To make up for the lack of thermodynamic data, some updating is required. However, this procedure depends on the experimental measures available in the literature which are unfortunately very scarce for these systems and particularly for K_2O.

An experimental approach has been used in this paper to get a liquidus temperature measurement and to compare it with the calculation. The experiments have been carried out with and without sealed capsules.

Without capsules, the first system studied is the ternary $K_2O-CaO-SiO_2$ (KCS), which made it possible to validate the method used thanks to the comparison with existing literature data. Very little K_2O is volatilized. However a 200 °C discrepancy with calculation (Table 11) confirms the lack of optimization of the FToxid database as previously discussed. This experimental method (without capsule) has been applied to the multi component composition C1 containing seven oxides. This result has given a first approximation of the liquidus temperature for C1, which has been confirmed by measurement with the sealed capsule method. Because of the large differences with the calculation (~100 °C), the lack of optimization (for FToxid database) is again confirmed.

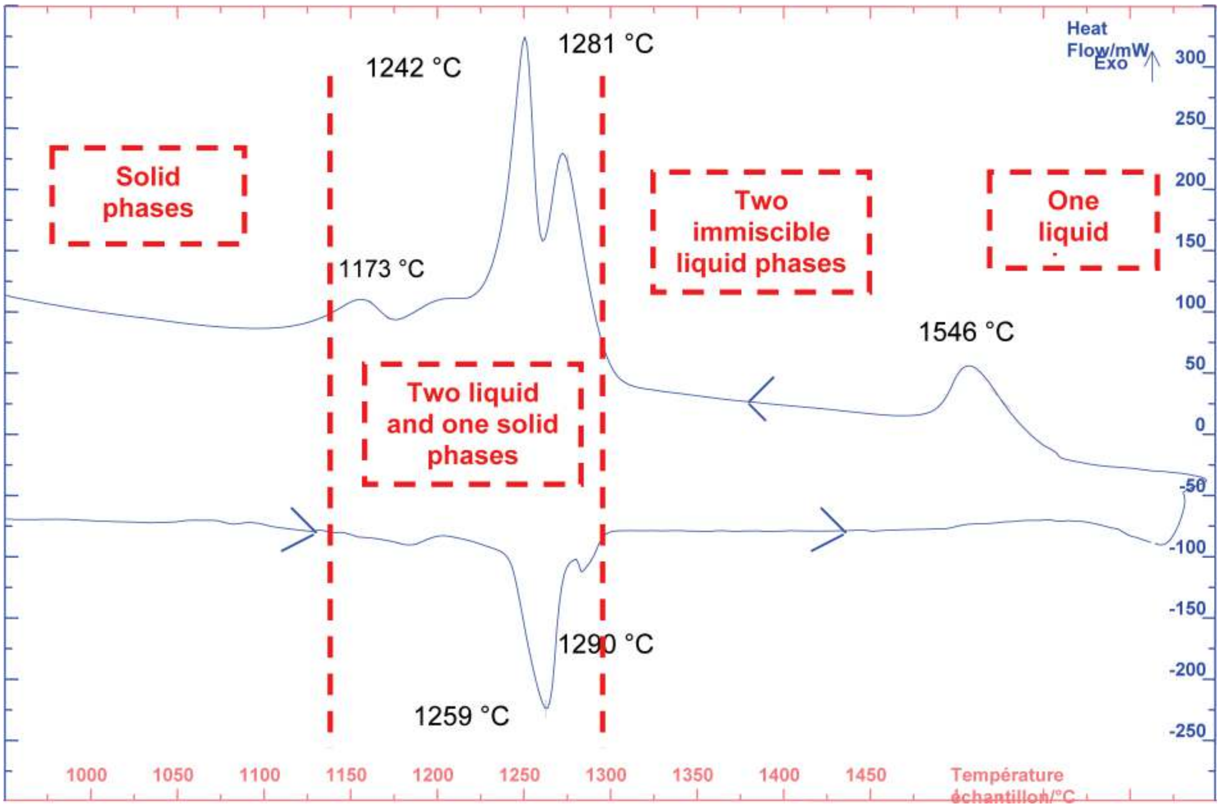


Figure 18. Differential scanning calorimetry (DSC) of C2 (under argon, T_{max} = 1600 °C).

Table 11. Liquidus Temperatures for KCS, C1, and C2

	thermodynamic calculations	experimental measurements
KCS	1418 °C	$1225 < T_{\text{liquidus}}$ (°C) < 1230
C1	1342 °C, with alkalis	$1235 < T_{\text{liquidus}}$ (°C) < 1240, without capsule $1228 < T_{\text{liquidus}}$ (°C) < 1234, with capsule
C2	1420 °C, without alkalis no miscibility gap in the liquid phase 1256 °C, with alkalis presence of miscibility gap	$1372 < T_{\text{liquidus}}$ (°C) < 1376, without capsule, that is, without alkalis no miscibility gap in the liquid phase $1230 < T$ (°C) < 1295, with capsule, that is, with alkalis disappearance of the solid phase, presence of miscibility gap

Besides, the primary crystallization phase predicted is not in agreement with the one experimentally obtained and no miscibility gap in the liquid phase is observed experimentally contrary to calculations.

This procedure without capsule could not be applied for the multicomponent C2 composition, which is richer in K_2O than C1. Because of K_2O volatilization with increasing temperature, all the K_2O is volatilized at the liquidus temperature of C2 (1375 °C). Nevertheless, these experimental results are in agreement with thermodynamic predictions for composition without alkali species. The liquidus temperatures are reasonably close (Table 11). There is a difference of less than 50 °C, and the primary crystallization phase is wollastonite as calculated. This result validates the FToxid database without alkali species as already observed by Jack.[15,16]

For the composition C2, the use of capsule gave reliable results. The liquidus temperature ranges between 1230 and 1295 °C and no K_2O loss has occurred. The samples exhibit also the formation of two immiscible liquid phases. This is in agreement with thermodynamic predictions (1256 °C) taking into account alkali species. The good accordance between thermodynamic calculations and measurements for this C2 multicomponent composition is very surprising because this composition is richer in K_2O and because the FToxid database has been found to be poorly validated when alkalis are present. Thus, it should not be concluded that the FToxid is well validated for this C2 ash. Indeed, one must conclude that an opposite effect might be compensated in the database.

5. Conclusion

This paper has shown a good agreement between thermodynamic calculations and measurements of liquidus temperatures and primary phases of crystallization for ashes without alkali as already observed in the literature.[15,16] However the discrepancy between the measured and calculated liquidus temperatures of systems containing alkalis (K_2O) is between several hundred and 0 °C. 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 FToxid database where alkalis are present as it is clearly indicate in the F*A*C*T instructions. However, the literature provide too few measurements that can be taken into account by the FToxid database developers. Such measurements with alkalis are not easy to perform because of their high volatility. Nevertheless an experimental set up has been presented in this paper which is able to produce reliable results with binary or ternary systems and multicomponent systems (7 oxides). Only the ternary result presented in this paper could be taken into account to improve the database. The two multicomponent compositions C1 and C2 measured in this study can only be used to validate a thermodynamic database as too many oxides are present and some compensation error may occur as is probably the case with the composition C2.

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