



An approach to the heating dynamics of residues from greenhouse-crop plant biomass originated by tomatoes (*Solanum lycopersicum*, L.)

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Abstract

The most representative of greenhouse-crop plant biomass residues of tomatoes (*Solanum lycopersicum* L.) were selected for this study by using X-ray fluorescence spectrometry (XRF) and X-ray powder diffraction (XRD). The heating dynamics in air in the 600–1150 °C range of these residues for the production of renewable energy and the resultant ashes have been investigated. A total of 11 elements were determined by XRF in the biomass ashes and some minor elements. The content of alkaline elements and chlorides decreased as increasing heating temperature and disappeared at 1150 °C. Alkaline salts, NaCl and KCl, were volatilized by heating since 800 °C. The total contents of S and P in the biomass ashes were associated to CaSO₄, and a complex phosphate identified by XRD. CaCO₃ present at 600 °C was decomposed to CaO with disappearance at 1000 °C. By heating, new silicates were formed by solid-state reactions in the biomass residue. The minor elements have been found in a relative proportion lower than 0.9 wt.% and they characterized the obtained ashes, with potential use as micronutrients.

Keywords Biomass residues · Greenhouse-crops · Tomatoes · Heating transformations · XRF chemical analysis · Heating dynamics

Introduction

The global growth of biomass has been estimated between 112 and 220 billion tonnes per year (Vassilev et al. 2013a; Vassilev et al. 2013b). The production of biomass, with potential energy applications, has been estimated between 1.1 and 3.1 billion tonnes per year for agricultural residues. Biomass is particularly important in rural areas, commonly the most accessible and cheapest energy resource (Demirbaş 2004). Agricultural residues have been investigated for combustion and gasification (Arvelakis et al. 1999). Thus, residues

such as cotton gin wastes and grape residues have been of interest, with additional studies of fractionation and leaching (Arvelakis et al. 2003). Decomposition of biomass samples has been widely reported in the literature, for instance sawdust (Strezov et al. 2003), olive wastes (Nogales et al. 2011), and wood pellet (Febrero et al. 2014). However, it should be noted that heating transformations of biomass has not been considered.

Research on the combustion process of biomass (wood and oat) and sewage sludge have been also interesting subjects of previous research (Magdziarz and Wilk 2013). Characterization and comparison of biomass ashes from wood pellet, with different thermal histories, have been reported (Febrero et al. 2014). The elemental composition of wood ashes, obtained by the combustion of wood, has been determined by analytical techniques (Górecka et al. 2006). These wood ashes may find a potential application as deacidifying agents and soil conditioners, but in this last case, additional supplementation with nitrogen fertilizer would be necessary. An experimental approach has been proposed in agricultural biomass to study the chemical and physical properties of the ash (Cioabla et al. 2015). A characterization of inorganic matter in vegetable biomass feedstocks has been also investigated (Suárez-García et al. 2002). Magdziarz et al. (2016a, 2016b)

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reported the chemical composition, character, and reactivity of renewable fuel ashes and their impact on fouling and slagging during combustion. In all the studies above summarized, a variety of analytical techniques have been used. In accordance with Cereda et al. (1995a), the understanding and optimization of combustion processes as well as the development and improvement of emission control devices can be significantly enhanced by a full knowledge of the chemico-physical properties of the combustion products. In this sense, major and trace element characterization of coal fly ash particles and coal combustion have been reported (Cereda et al. 1995a; Cereda et al. 1995b; Bogdanović et al. 1995).

On the other hand, the cost of the biomass and waste gasification by developing sustainable and economical methods is an urgent need, even for ash utilization and management (Fernández-Pereira et al. 2011). In previous research (Marcelis et al. 1989; Marcelis 1993), simulation studies of dry matter distribution and biomass allocation in greenhouse crops have been reported. In Spain, the area occupied by greenhouses and macrotunnels has more than 56,000 ha, being the 70% of these located in SE Spain (Callejón-Ferre et al. 2011). The province of Almería is the most important zone with more than 27,000 ha with production of tomatoes, lettuces, aubergines, courgettes, peppers, cucumbers, melons, and water melons (Callejón-Ferre et al. 2009, 2010, 2011, 2014). Evidently, the formation of large amounts of crops residues is a problem, with estimations of greenhouse crop plant residues more than 235,000 t/year (Callejón-Ferre et al. 2009, 2011). For this reason, investigations on the production of renewable energy using these residues are of great interest. Callejón-Ferre et al. (2009, 2010, 2011, 2014) studied greenhouse crop residues as a source of renewable energy. They proposed mathematical models to predict the higher heating values of crop residues (Callejón-Ferre et al. 2014). It should be noted that the plant remains of tomatoes (*Solanum lycopersicum* L.) are the highest of all the biomass produced by the greenhouse crop agricultural industry in Almería, with 49 t/(ha year) and a total dry biomass of 250,127 t/year. The energy potential of the greenhouse crop wastes has been computed in 1,003,497.97 MWh/year from the direct higher heating value calculations (Callejón-Ferre et al. 2014). Then, it is very interesting to perform research on greenhouse crop plant biomass as a renewable and sustainable source of energy. Thus, in a recent investigation by the authors (Morales et al. 2017), a thermal study of residues from greenhouse crop plant biomass originated by the remains of tomatoes was reported (*Solanum lycopersicum* L.).

The aim of this work was to investigate the variations in chemical composition of ashes coming from the thermal treatments and heating transformations of greenhouse crop plant biomass residue. According to previous reports (Bogdanović

et al. 1995, Somerset et al. 2004), an analytical technique has been investigated for being capable of determination of elements in a solid sample by X-ray fluorescence spectrometry (XRF).

Experimental

Sample and sample preparation

The greenhouse crop plant biomass residues used for the present investigation were selected from an integral industrial processing plant of agricultural residues (Níjar, Almería, Spain). These residues, with high relative proportions of lignin, cellulose, and hemicellulose, are mainly constituted by crop species of tomatoes (*Solanum lycopersicum* L.). The industrial plant produced a residue with a particle size lower than 25 mm using a steel screen, with 25 mm openings. Representative samples were received at the laboratory, homogenized, and air-dried for 48 h. After this, they were also dried using an oven at 110 °C.

Thermal treatments of the samples were performed using a laboratory furnace (muffle Hobersal, model HD-230) with a microprocessor (West 6100). A heating rate of 20 °C min⁻¹ in static air was used in all the thermal treatments. The crucibles were made of sintered high-alumina to avoid any thermal interaction with heated samples. The crucibles with sample (1–2 g) were introduced into the furnace at room temperature and heated in air at 20 °C min⁻¹ up to 250 °C, with a holding time of 60 min. After this time, the temperature of the furnace was raised to 600–1150 °C and hold during 120 min. In a recent paper, these variations using thermal and elemental analysis were studied (Morales et al. 2017). The effects of heating cycle were remarked, considered temperature and holding times. After these thermal treatments from 600 to 1150 °C, the crucibles with the ashes were cooled into the furnace up to 100 °C and then they cooled prior to further characterization.

Bulk elemental analysis using XRF spectrometry

XRF spectrometry was applied to investigate the variation in chemical composition of the greenhouse crop plant biomass residues after thermal treatments. Following a protocol, the samples were previously dried, weighed, and heated in air using a furnace (Nabertherm, model L15/11/P320) from room temperature to 1025 °C in porcelain crucibles. This temperature was reached in 1 h and 40 min and was hold during 3 h. Then, the samples were cooled into the furnace, recorded the mass variation, ground, and the resultant powders were prepared as pressed pellets using boric acid. The equipment for XRF spectrometry was an Axios PANalytical B.V. Wavelength Dispersive Spectrometer. The X-ray tube was a

super-sharp end-window tube with Rh standard anode, ceramic insulation, and ultra-high transmission. The experimental conditions were the same as in a previous research (Garzón et al., 2009, 2017). Eleven major elements (in alphabetic order) Al, Ca, Fe, K, Mg, Na, P, Si, and Ti along with Cl and S were determined. Several minor elements (Br, Cr, Cu, Mn, Mo, Rb, Sr, and Zn) were also determined. The quality of the analytical results concerning their precise and accurate characteristics was checked by measurements using geological standard certified materials of the International Association of Geoanalysts, recommended after proficiency tests for analytical geochemistry laboratories (de Sena et al. 1995). Iron content as Fe_2O_3 for the standards was given as Fe_2O_3 Total (Fe_2O_3 T).

X-ray diffraction analysis

The phase composition of the samples after thermal treatments was determined by XRD analysis. Samples were scanned in random preparations using a diffractometer X'PERT PRO of PANalytical, with Ni-filtered $\text{CuK}\alpha$ X-ray radiation, graphite monochromator, at 36 kV and 26 mA, and a scanning speed of 1° in 2θ min^{-1} from 3 to $70^\circ 2\theta$. The crystalline phase analysis was determined using the X-ray diagnostic peaks of each mineral phase by identification using the computer program provided with the equipment, providing a calculation of relative phase percentages to compare the heated samples. The sources of errors in this calculation that influence the shape of XRD peaks, such as preferred orientation, background, and effect of intensive grinding on the samples, were avoided (Niskanen 1964; Sánchez-Soto et al. 1993; Garzón and Sánchez-Soto 2015).

Results and discussion

Chemical composition by XRF spectrometry of samples of greenhouse crop plant biomass residues is presented in Tables 1, 2, 3, and 4. Table 1 shows the major elements, expressed as oxides, except Cl and Table 2 shows these elements on a calcined basis. Table 3 shows the results of XRF determination of some minor elements, expressed as oxides, except Br and Table 4 shows these same results on a calcined basis.

As was expected, the weight variation after heating, considered the “loss on ignition” (LOI, in wt.%), decreased in the samples as increasing the heating temperatures. These weight variations are associated with the thermal decomposition of the biomass residues by pyrolysis and combustion in air with elimination of water and volatile compounds originated from the degradation of the organic matter. In fact, during heating, the organic matter and inorganic minerals (as instance, clay minerals such as illite or muscovite, carbonates, halides,

Table 1 XRF results (in weight %) of greenhouse crop plant biomass residues treated at different temperatures in the range 600–1150 °C

wt.%	L600	L800	L1000	L1150
CaO	19.88	25.41	38.50	38.59
SiO_2	3.50	5.24	12.58	16.92
MgO	6.32	8.75	18.17	16.88
SO_3	5.37	7.09	12.16	11.19
P_2O_5	2.31	3.23	6.28	5.96
Al_2O_3	1.02	1.32	3.15	3.83
Fe_2O_3 T	1.06	1.16	1.85	2.48
Cl	9.09	10.05	1.80	0.63
TiO_2	0.18	0.15	0.31	0.38
K_2O	8.86	7.72	0.12	0.07
Na_2O	2.48	3.02	0.16	0.06
LOI	39.39	25.97	3.26	1.10
Total	99.46	99.11	98.34	98.09
CaO/MgO	2.26	2.45	1.99	1.56
Cl/S	4.22	3.53	0.37	0.14

sulfides, etc.) undergo several complex physico-chemical reactions in air, such as oxidation, reduction, dehydration, dehydroxylation, carbonization, decomposition, etc.). The values of LOI are progressively lower from 600 °C, reaching 3.26 wt.% at 1000 °C, and 1.1 wt.% at 1150 °C (Table 1). The pyrolysis and combustion reactions are initiated from lower temperatures. The previous results by thermogravimetric analysis (at a low heating rate of 6 °C/min in air) indicated that the weight variations are very fast from 150 to 300 °C and reached 70–90 wt.% of weight loss from 300 to 500 °C (Morales et al. 2017). Cleaner and light white ashes, with elimination of

Table 2 XRF results of Table 1 (in weight %) on a calcined basis

wt.%	L600	L800	L1000	L1150
CaO	32.78	34.35	39.81	39.01
SiO_2	5.77	7.08	13.00	17.10
MgO	10.42	11.83	19.20	17.06
SO_3	8.85	9.58	12.57	11.31
P_2O_5	3.81	4.36	6.49	6.02
Al_2O_3	1.68	1.78	3.25	3.87
Fe_2O_3 T	1.65	1.56	1.91	2.50
Cl	14.98	13.58	1.86	0.63
TiO_2	0.29	0.20	0.32	0.38
K_2O	14.61	10.43	0.12	0.07
Na_2O	4.08	3.02	0.16	0.06
Total	98.92	97.77	98.69	98.01
CaO/MgO	3.14	2.9	2.07	2.28
Cl/S	4.23	3.54	0.37	0.14
CaO/ P_2O_5	8.60	7.88	6.13	6.48
MgO/ P_2O_5	2.73	2.71	2.95	2.83

Table 3 XRF results (minor elements in weight %) of greenhouse crop plant biomass residues thermally treated at different temperatures

wt.%	L600	L800	L1000	L1150
SrO	0.236	0.296	0.485	0.508
Cr ₂ O ₃	0.014	–	0.043	0.291
MoO ₃	0.105	0.150	0.195	0.195
MnO	0.064	0.051	0.142	0.116
CuO	0.025	0.037	–	0.025
ZnO	0.025	0.025	0.037	0.025
Br	0.070	0.070	–	–
Rb ₂ O	0.011	0.011	–	–
Total	0.550	0.640	0.902	1.160

Note: The indication – means “below equipment limit detection”

elemental carbon, are progressively formed by heating. These results reflect the dynamics of heating the biomass residues. In fact, the elemental analysis (average results) of the original biomass residue was C = 44.37 wt.%, H = 5.91 wt.%, N = 0.75 wt.%, and O = 39.77 wt.% with a carbon content of 6.21 wt% after heating the biomass sample at 600 °C, which decreases to 1.91 wt.% at 800 °C and 0.70 wt.% after heating the sample at 1000 °C (Morales et al. 2017). Some part of the organic matter of the sample is eliminated by pyrolysis and combustion reactions when the sample is heated at 600 °C and higher. An additional weight loss can be associated to dehydration and volatile emissions.

The main elements identified in the progressive formation of ashes by heating are CaO, MgO, SiO₂, and SO₃ (Tables 1 and 2). The organic matter decreased by heating effect that produces its elimination, as pointed out above, and the inorganic content increased in particular after heating at 1150 °C. For instance, CaO reaches 38.59 wt.%, MgO 16.88 wt.%, and SiO₂ 16.92 wt.%. They could be associated to the formation of carbonates or phosphates in the ashes. Reaction of the resulting basic oxides (CaO, MgO) with acidic gases from thermal decomposition will form stable salts, such as sulfates

Table 4 XRF results of Table 3 (in weight %) on a calcined basis

wt.%	L600	L800	L1000	L1150
SrO	0.389	0.400	0.501	0.513
Cr ₂ O ₃	0.023	–	0.044	0.294
MoO ₃	0.173	0.203	0.201	0.197
MnO	0.105	0.068	0.146	0.117
CuO	0.041	0.050	–	0.025
ZnO	0.041	0.033	0.038	0.025
Br	0.115	0.094	–	–
Rb ₂ O	0.018	0.018	–	–
Total	0.905	0.866	0.930	1.171

Note: The indication – means “below equipment limit detection”

and phosphates. The CaO/MgO ratio is 2.29 at 600 °C, which changes to 1.56 at 1150 °C (Table 1), with values of 3.14 and 2.28, respectively, on a calcined basis (Table 2).

The total iron content, as Fe₂O₃ T, increases from 1.06 to 2.48 wt.% as maximum although it is not as free iron oxide because the ashes, with elimination of carbon, are progressively cleaner and light white. The increase in some percentages of elements can be also observed for non-metal elements sulfur and phosphorus (as SO₃ and P₂O₅, respectively). The content of SO₃ is relevant, with an increase from 5.37 wt.% at 600 °C to 11.19 wt.% at 1150 °C, practically twice. Possibly, S and P could be combined forming stable sulfate and phosphate compounds, as found in other biomass ashes (Vassilev et al. 2013a; Vassilev et al. 2013b).

The content of the alkaline (K and Na) elements (as oxides) is relatively high at 600 °C, although K₂O is higher than Na₂O. Their contents decrease as increasing the heating temperatures from 600 to 1000 °C. It can be seen better with the results on a calcined basis (Table 2), with changes of 14.61 wt.% of K₂O and 4.08 wt.% of Na₂O at 600 °C to 0.07 and 0.06 wt.%, practically the same value, which are reached at 1150 °C. It is remarked that the content of Cl at 600 °C is of 14.98 wt.% (Table 2) and it decreases also by heating, reaching 0.63 wt.% at 1150 °C. In consequence, there is a loss of K, Na, and Cl by heating. According to previous results of the literature (Vassilev et al. 2013a; Vassilev et al. 2013b; Etiegni and Campbell 1991), it can be noted that the content of K and Na decrease when carbonates are formed, being associated to their low boiling point and decomposition.

The behavior of other biomass residues converted in ashes produces weight losses in the temperature range 800–1050 °C, associated to a higher release of KCl by the heating (Vassilev et al. 2013b; Arvelakis et al. 2003). It should be noted that ash from agricultural biomass combustion contains 3–20 times lower concentration of heavy metals than ashes produced from the wood biomass (Cioabla et al. 2015). If the alkaline elements are combined as halides, such as chlorides, then the sublimation of KCl (sylvite) occurs at 815 °C (Suárez-García et al. 2002). In fact, alkali metal chlorides can vaporize in the temperature range 770–900 °C (Arvelakis et al. 2003). In this sense, the same can be suggested for Br (Table 3), because alkaline bromides (as similar halides containing Cl) could be formed in the biomass ashes by heating and volatilized when the sample is further heated. For this reason, the content of Br decreases after thermal treatment from 600 °C and higher.

The volatilization of elements, such as K, Na, Cl, and Br, although combined as halides, has been reported in the literature (Vassilev et al. 2013a) and associated with organic matter as a result of biomass combustion. The review of Vassilev et al. (2013a) shows the mean and range contents of elements volatilized from biomass during combustion (in wt.%). The same phenomenon of volatilization of alkaline chlorides can occur in the present case when the greenhouse crop plant

biomass residues are being heated, in particular from 600 to 1150 °C (Table 1). The content of elements coming from the formation of wood ashes, such as K and Na, decreased in woods from 500 to 1400 °C (Misra et al. 1993). Other elements, such as Si, Fe, and Ca, kept constant. In other reports (Febrero et al. 2014), it was found that Cl is almost completely removed by thermal treatments forming ashes below 550 °C. Combined chlorides almost disappear in the ash process.

It is interesting to see the CaO/P₂O₅ and MgO/P₂O₅ ratios as included in Table 2 on a calcined basis. A decrease of the ratio concerning CaO/P₂O₅ can be observed, and, at the same time, the values of the ratio MgO/P₂O₅ almost kept constant at any temperature in the temperature range 600–1150 °C. This result suggests a possible combination between the elements Mg and P due probably to sulfate formation.

Another interesting feature deduced by XRF analysis is the ratio Cl/S. A few investigations have reported the effects of alkali metals, chlorine, and sulfur during combustion of biomass because they can cause serious corrosion problems in the biomass reactors (Cioabla et al. 2015; Król and Poskrobko 2012; Magdziarz and Wilk 2013). According to these previous investigations, this ratio must be lower than 0.454 to avoid corrosion in the structural elements of the boilers. The present results (see Tables 1 and 2) indicate that this Cl/S ratio is 0.37 at 1000 °C and 0.14 at 1150 °C, being lower than 0.454. Taking into account the present results, the greenhouse crop plant biomass residues studied in this paper, besides their processing in pyrolysis or gasification, can be suitable for combustion in power plants.

On the other hand, the chemical analysis by XRF spectrometry of some minor elements (expressed as oxides), as found in the biomass residues after thermal treatments in the range 600–1150 °C, is presented in Tables 3 and 4. The total sum is lower than 0.9 wt.%. They characterize the resultant ashes and, in general, their content increases as increasing heating temperature. Some elements are not relevant, such as Rb₂O or CuO or even ZnO, the last almost is kept constant. However, MnO, MoO₃, and SrO increase as increasing the heating temperature. In particular, SrO must be in relation with CaO and MgO (see Tables 1 and 2). These all minor elements are interesting for sustainable ash utilization, for instance when micronutrients are examined to apply the ashes as soil conditioners (Górecka et al. 2006).

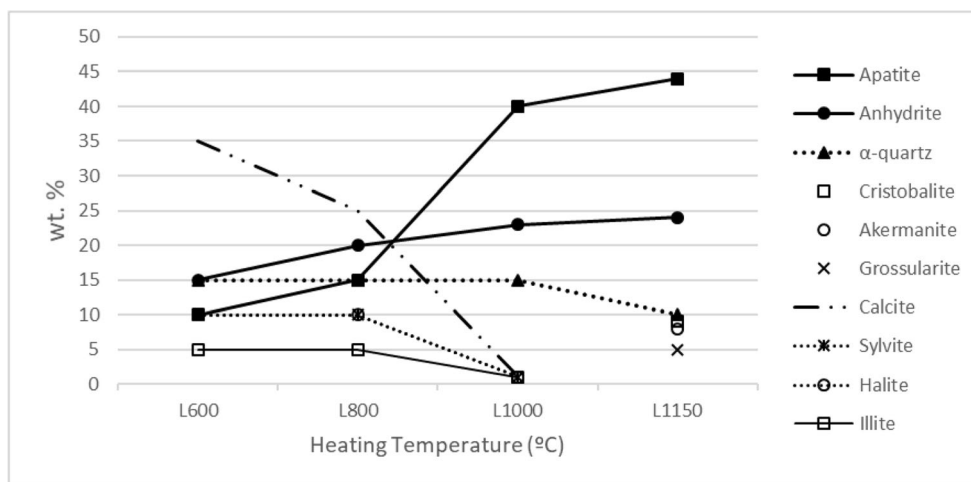
The XRD analysis allowed the identification of the main crystalline phases originated by thermal treatments of the biomass residues in the range 600–1150 °C (Fig. 1). Taking into account a previous review (Vassilev et al. 2013a; Vassilev et al. 2013b), approximately 229 forming major, minor, and accessory phases of minerals were identified in biomass ash according to the literature. Thus, it can be difficult to study the behavior of phase formation and evolution produced in a variety of biomass ashes, the solid residue which results from the combustion of biomass, as a function of different thermal treatments.

At 600 °C, calcium salts have been identified as carbonate and sulfate, mainly calcite (CaCO₃) and anhydrite (CaSO₄). This result is in accordance with the high percentage of CaO deduced by XRF analysis (Tables 1 and 2). A clay mineral, illite or muscovite, has been also identified by XRD in a low relative proportion, although it must be as a dehydroxylated clay mineral phase according to previous results (Udagawa et al. 1974; Sánchez-Soto et al. 2007). Silicon dioxide (silica, α-quartz) is present in the biomass residues heated at 600 °C. Illite and silica could be a contamination of the residue present as mineral soil components of the crop species of tomatoes (*Solanum lycopersicum*, L.) and the origin is assumed not produced by heating the biomass residues. Alkaline salts sylvite (KCl) and halite (NaCl) are also identified in these heated samples. A crystalline and complex phase containing phosphorus is also identified by XRD: the phosphate apatite, although with a variable chemical composition containing Ca, Mg, and Na [(Ca_{3.892}Na_{0.087}Mg_{0.021})(Ca_{5.599}Na_{0.125}Mg_{0.029})(PO₄)_{5.5}].

These results are consistent with previous chemical analysis by XRF spectrometry (Tables 1 and 2). Samples treated at 800 °C show a similar phase composition as described above, although the relative percentages are distinct. Calcite (CaCO₃) content decreases by thermal decomposition producing CO₂ and CaO. Apatite phosphate and anhydrite increase in relative proportion as increases heating temperature. The more relevant changes can be deduced by XRD when the biomass residues are treated above 800 °C. Calcite is totally decomposed at 1000 °C with an increase in apatite content. Quartz relative proportion is almost kept constant at 1000 °C. However, dehydroxylated illite and the alkaline salts, mainly sylvite (KCl) and halite (NaCl), disappeared above 1000 °C. In the case of dehydroxylated illite, it is associated to thermal decomposition producing free silica and alumina ready to solid-state reactions with other ash components, for instance CaO or iron oxide. These solid-state reactions will form distinct compounds by thermal transformation, as identified at higher temperatures.

Finally, at 1150 °C, apatite shows the highest content, with medium of anhydrite and new crystalline phases are detected by XRD: the high-temperature silicates akermanite (Ca₂MgSi₂O₇) and grossularite (Ca₃Al_{1.332}Fe_{0.668}Si₃O₁₂). A polymorph of silica, cristobalite (SiO₂), is also detected possibly by conversion from α-quartz (Perrotta et al. 1989; Stevens et al. 1997). It should be noted that cristobalite and these two silicates are not detected before 1000 °C, or they are in a low relative proportion to be identified by XRD techniques. Phases named akermanite and grossularite could be originated by solid-state reactions between MgO and CaO with silica and dehydroxylated illite, besides iron oxide (Tables 1 and 2) in the case of grossularite.

Fig. 1 Evolution of crystalline phases (in wt.%) determined by XRD in the biomass ashes produced by heating temperature in the range 600–1150 °C



According to the present results of the phase evolution, a *Scheme* of the main changes in chemical and phase composition of heating dynamics is depicted as follows:

- (1) non-stable crystalline phases identified at 600–800 °C in the resultant ashes: alkaline halides (mainly sylvite KCl and halite NaCl), calcite (CaCO₃), and dehydroxylated illite. Heating dynamics produces volatilization (K, Na, Cl, and Br combined as halides) and decomposition (calcite).
- (2) stable crystalline phases identified at any temperature in the range 600–1150 °C: anhydrite (CaSO₄) and apatite phosphate with a variable chemical composition containing Ca, Mg, and Na, besides α-quartz.
- (3) new-formed crystalline phases by solid-state reactions at higher temperatures than 1000 °C: akermanite (Ca₂MgSi₂O₇), grossularite (Ca₃Al_{1.332}Fe_{0.668}Si₃O₁₂), and cristobalite (SiO₂). The last phase is formed by partial thermal conversion from α-quartz.

It should be noted that detection of α-quartz by XRD has been reported in biomass ashes, besides calcite, anhydrite, sylvite, various other Ca-, Mg-, Na-, and K-containing phases and different phosphates as inorganic constituents of the other biomass residues after heating (Arvelakis et al. 2003; Febrero et al. 2014; Suárez-García et al. 2002; Vassilev et al. 2013a; Vassilev et al. 2013b). Chemical and phase changes, as evidenced in this work, indicate that the study of only a single temperature concerning the production of biomass ashes (in this case, tomatoes *Solanum lycopersicum*, L.) is not enough because both chemical and phase variations are important in the formation of the biomass ashes.

Taking into account the report by Duminuco et al. (1998), the relationships among phases formed during the firing process of mineral clays indicate that their composition is related to the composition of precursor phases on which they grow. Even some variations in microtextures of heated products

have been reported (Duminuco et al. 1998). Finally, in an approach to study “the dynamics of clay firing”, Riccardi et al. (1999) pointed out that reactions during firing occur following two main mechanisms: (i) reactions leading to nucleation and growth of new mineral phases (“modal reactions”) and (ii) reactions producing only compositional variations of phases (“cryptic reactions”). The results obtained by XRD (Fig. 1) evidenced the complex interactions on these biomass residues between decomposed crystalline phases and the formation of new crystalline phases, as influenced by the thermal treatments. However, using four temperatures (600, 700, 1000, and 1150 °C), such as in the present study, it is possible to analyze the formation and evolution of crystalline phases by XRF complemented with XRD.

Conclusions

The heating dynamics of greenhouse-crop plant biomass residues at high temperatures has been investigated, mainly constituted by tomatoes (*Solanum lycopersicum* L.), for the production of renewable energy, using an approximation of variations in chemical analysis (XRF) complemented by phase analysis (XRD) in the range 600–1150 °C, with holding times of 2 h. The heating dynamics produced that the values of weight loss by thermal treatment decrease progressively with the increasing of temperature by several complex reactions (i.e., oxidation, decomposition, etc.), forming cleaner and light white ashes.

A composition dependence of heating treatment of these greenhouse-crop biomass residues has been found. The elements Ca, Mg, Si, and S (in this decreasing order) presented the higher proportions in the ashes. The alkaline elements were also present, being the ashes obtained at 600 °C enriched in K₂O, with 14.61 wt.%, and contents of Na₂O 4.08 wt.%, with 14.98 wt.% of Cl (all the results on a calcined basis). However, the content of K, Na, and Cl decreases as increasing

the temperature of treatment from 600 to 800–1000 °C, with disappearance above 1000 °C. The biomass ash obtained after thermal treatment at 1150 °C is light white in color. It contains 39 wt.% CaO, 17 wt.% of MgO and SiO₂, 11 wt.% SO₃, 6 wt.% P₂O₅ and ~4 wt.% Al₂O₃, showing contents of Fe₂O₃ T of 2.5 wt.% and lower contents (<0.4 wt.%) of Cr₂O₃ and TiO₂. The minor elements have found in a relative proportion lower than 0.9 wt.% and they characterized the obtained ashes, with potential use as micronutrients.

The changes in chemical composition of the heated samples have been related to the phase variations. Phase analysis demonstrated that alkaline salts sylvite (KCl) and halite (NaCl) are formed, but the volatilization by heating these chlorides from 800 °C produced this effect of loss of K, Na, and Cl. The contents of S and P have been associated to combined salts: anhydrite (CaSO₄) and a complex calcium phosphate (apatite), both crystalline phases showing the higher proportion at 1000 and 1150 °C. The ratios CaO/P₂O₅ and MgO/P₂O₅, the last almost constant, agree with the formation of apatite phosphate-containing Mg in its crystal structure. Calcite (CaCO₃) was also identified at 600 °C, but the decomposition of this carbonate by progressive heating should give rise to CaO for solid-state reactions with SiO₂ and decomposed dehydroxylated illite. The biomass residue heated at 1150 °C produces new silicates akermanite and grossularite, and the conversion of a part of silica to its polymorph cristobalite.

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