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Analytical pyrolysis of fir sawdust, olive stone and sewage sludge in molten carbonate salts

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ABSTRACT

Py-GC-MS was applied to study the chemical composition of semivolatile pyrolysates evolved from fir wood sawdust, olive stone and sewage sludge, in the presence of molten Li_2CO_3-Na_2CO_3-K_2CO_3 salt. The effects of pyrolysis temperature from 400 to 800 °C and salt content (2.5, 5 and 10 times the biomass) were investigated utilising a semi-quantitative approach. Carbonate molten salts inhibited the generation of pyrolysis products from cellulose(anhydrosugars, pyranes, hydroxyacetaldehyde) with the exception of pentacyclic ketones (e.g. 2-cyclopenten-1-ones). The molten salts did not affect considerably the pyrolytic pattern of alkylated phenols, guaiacols and syringols from lignin, but lowered significantly the occurrence of monomers with oxygenated side chains (e.g. vanillin, syringaldehyde) and dimers. The production of catechols was inhibited by molten carbonates at 400–500 °C, but increased at higher pyrolysis temperatures. The marked decrease of pyrolysis products evolved from fir wood and olive stone in the presence of salts was not observed for sewage sludge. The pyrograms of sewage sludge were characterised by amines from proteins (indoles, pyrroles, diketopiperazines) even at high salt content. Steroids, dominated by thiocholestane and thiostigmastane, featured the lipid fraction of sewage sludge without and with molten salts. The production of aromatic hydrocarbons increased significantly with increasing pyrolysis temperature at expenses of oxygenated constituents.

1. Introduction

Molten salts, eutectic mixtures with lower melting points compared to single salts, have attracted increasing attention in the renewable energy sector due to their characteristics of high permeability and low viscosity which can improve the heat transfer and degradation of biomass during pyrolysis compared to conventional pyrolysis [1–3]. One promising approach involves incorporating molten salts to produce a liquid reaction medium during the thermochemical transformation of biomass. In this process, molten salt serves as a multifunctional medium, simultaneously acting as heat carrier, ionic solvent and catalyst promoting the breakdown of complex macromolecules for the conversion into useful materials or specific chemicals in thermal treatment processes [1,2].

Factors such as the chemical and thermal stability of molten salts and thermal melting characteristics play a crucial role in assessing the suitability of various types of molten salts for biomass pyrolysis. Alkali metal cations, especially K^+, are known for their catalytic activity [4–9]. Thus, LiNaK were commonly used to prepare eutectic salts of carbonates, nitrates, sulphates and chlorides; these salts were preferred over phosphates, borates, silicates as they do not form glassy materials [2]. Alkali metal chlorides have been often used in combination with $ZnCl_2$ to improve the reactivity of molten salts and increase the yields and/or quality of bio-oil [10–12]. Volatilisation of chlorides, formation of HCl and chlorinated organic compounds are potential drawbacks [11].

Alkali metal nitrate salts were investigated as reactive medium for the pyrolysis of biomass at temperatures of 300 °C with $NaNO_3$-KNO_3-$NaNO_2$ (the mixture used in concentrated solar power applications) [13] and with $NaNO_3$-KNO_3 at 500 °C [14]. At higher pyrolysis temperatures nitrate salts decompose, thus carbonates are more suitable for pyrolysis

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of biomass at temperatures higher than 600 °C [15]. In particular, the ternary mixture Li_2CO_3-Na_2CO_3-K_2CO_3 is well suited for investigation in a wide range of pyrolysis temperatures being characterised by a low melting point (398 °C) and stability up to 900–1000 °C in the presence of CO_2 [15,16]. However, it should be considered that single carbonates above 700 °C decompose ($M_2CO_3 = M_2O + CO_2$) or react with char ($M_2CO_3 + C = M_2O + 2CO$) [16]. Slight weight losses of Li_2CO_3-Na_2CO_3-K_2CO_3 molten salt due to vaporisation and decomposition were reported around 12 % at 850 °C [10] and 5 % up to 1000 °C [15]. Pyrolysis of cellulose with NaK molten carbonates demonstrated high heating rates of particles causing efficient solid to gas conversion, improved formation of H_2 and CO, at the expenses of the condensable fraction [17].

In recent years, alkali metal carbonates were widely applied to study pyrolysis in the presence of molten salts of various biomass including cotton stalk [10,18,19], peanut shell [20], digestate [21,22], algae [23,24], lignin [25]. Most of the studies reported enhanced formation of non-condensable gas and reducing yields of liquid bio-oil from the pyrolysis of lignocellulosic biomass. Molten carbonate salts improved the characteristics of char [20]. Therefore, pyrolysis of biomass with molten carbonates is especially directed to the development of high performing carbon materials and gas, whereas bio-oil is inevitably formed as co-product to be allocated in downstream processes. The direct utilisation or upgrading of bio-oil will be dependent on its chemical composition which needs to be known for appropriate exploitations. Several studies on the analysis of bio-oil components have been conducted by GC-MS after solvent extraction and results expressed as peak area percentages [18,19,21]. This approach may cause bias for literature comparison due to the different solubility of pyrolysis products in organic solvents and uncertainty in molecular attribution when based solely on mass spectra library match.

Analytical pyrolysis, specifically Py-GC-MS, can provide preliminary and valuable information on the chemical composition of volatiles condensable into bio-oil irrespective of their solubility. At this regard, Estrada-Leon et al. have demonstrated the ability of analytical pyrolysis as a technique to understand the role of molten chloride salts in driving the chemical composition of pyrolysates evolved by lignocellulose biomass [11]. At the best of our knowledge, the effect of carbonate based molten salts have not been investigated yet by analytical pyrolysis. Moreover, the composition of bio-oil obtained from pyrolysis of sewage sludge with molten carbonate salts was not reported in the literature. The results are expected to provide prospective information on the chemical quality of bio-oil generated by carbonate molten salt pyrolysis.

The action of carbonate molten salts on the production of bio-oil with improved quality (less acidic and phenolic components) was described for lignocellulosic agricultural residues [10,18], while less information is available on forestry wastes and sewage sludge [1]. To the best of our knowledge, there are no examples of studies on bio-oil composition from pyrolysis of sewage sludge with molten carbonates in the literature. Molten LiNaK carbonates were investigated as media for the pyrolysis of sewage sludge with the aim of improving the quality of biochar, but information on the yield and composition of bio-oil was not reported [26].

The purpose of this research was to investigate the effect of LiNaK carbonate molten salts on the chemical composition of pyrolysates generated by different types of organic matrices. These were selected as a trade-off between diversity in chemical composition and their importance as organic residues to be valorised by thermochemical processes. Sewage sludge and agroforestry wastes are produced massively (in European Union, as an example, order of magnitude of Mton and Gton, respectively), therefore their valorisation by pyrolysis and even co-pyrolysis own significant interest [27]. Fir sawdust was selected to represent lignocellulosic matrix from residual forestry biomass (softwood), olive stone as an agricultural residue rich in lignin from angiosperms. Finally, sewage sludge was selected as an organic waste rich in proteinaceous and lipid components from microorganisms [28].

The influence of the relative amount of carbonate salts at 500 °C and the effect of pyrolysis temperature from 400 to 800 °C at the salt:biomass 5:1 ratio was investigated for each biomass.

2. Experimental

2.1. Materials and sample preparation

The used feedstock materials included fir sawdust (C: 46.7 %, H: 7.4 %, N: 0.08 %, O: 45.6 %, ash: 0.36 % w/d.b.), olive stone (obtained from a local olive mill C: 62.8 %, H: 7.1 %, N: 2.7 %, O: 26.9 %, ash: 0.48 % w/d.b), and sewage sludge (secondary sludge obtained from a municipal wastewater treatment plant; C: 22.0 %, H: 3.6 %, N: 3.2 %, S: 1.5 %, O: 33 %, ash: 36 % w/d.b).

The fir sawdust and olive stone were ground using an electrical grinder. The sewage sludge sample underwent a two-day drying process in an oven at 90 ℃ to eliminate all moisture content and crushed using a mortar. All samples were sieved at 0.3 mm.

Before conducting micropyrolysis experiments, the feedstocks underwent drying in an oven at 105 °C for 24 h. Equal quantities (2.0 g) of sodium, potassium, and lithium carbonate salts (Sigma Aldrich) were meticulously weighed, combined, and heated in the furnace at 600 °C for 2 h to ensure the formation of a homogenous eutectic liquid salt. The mass ratio 1:1:1 for Li_2CO_3:Na_2CO_3:K_2CO_3 (corresponding to the molar formula $Li_{0.9}Na_{0.6}K_{0.5}CO_3$) was selected from literature to aid comparison with bio-oil composition from bench scale reactors [10,18]. After cooling, the carbonate mixture was crushed well and then mixed with biomass in the following biomass:salt ratios 1:2.5, 1:5, and 1:10.

2.2. Py-GC-MS

Py-GC-MS was performed on about 0.7 mg of fir sawdust, 1 mg of olive stone and 0.9 mg of sewage sludge, alone or mixed with the appropriate quantity molten salt (2.5, 5.0 or 10 wt excess), poured into a Frontier Laboratories Ltd. stainless-steel cup (8 mm height and 4 mm internal diameter). Py-GC-MS analyses were carried out using a Frontier Lab pyrolyzer (EGA/PY-3030D) equipped with temperature-controlled reactors interfaced to a gas chromatograph (7890B Agilent Technologies)-quadrupole mass spectrometer (5977B Agilent Technologies). Pyrolyses were conducted at 500 °C for the different salt:biomass ratios and at temperatures 400, 500, 600, 700 and 800 °C for the salt:biomass 5:1 ratio.

Evolved products were introduced into the GC column through a Py-GC interface at 280 °C under 1:50 split conditions. The column was a fused silica capillary column (HP-5MS) 30 m × 0.25 mm id. and 0.25 µm film thickness of stationary phase 5 %-diphenyl and 95 %-dimethylpolysiloxane operated at 1.0 mL min^{-1} helium flow using the following thermal program: 50 °C for 2 min, then increased at 7 °C min^{-1} to 310 °C hold for 5 min. Mass spectra were recorded at a scan rate of 2.6 scans sec^{-1} with 70 eV electron ionization within the m/z 29–450 interval. The ion source and quadrupole temperatures were maintained at 230 °C and 150 °C, respectively.

2.3. Data handling

Identification of compounds relied on matching with the NIST 14 library and comparison with published mass spectra from Py-GC-MS (e.g. polysaccharide [29], lignin [30], cyclopentenones [31], proteins [32], steroids [33,34]). The lignin dimer (*E*)-4,4'-dihydroxy-3,3'-dimethoxystilbene was tentatively identified by comparison with published MS data of the isolated compound [35]. MS information is reported in Supplementary Materials (Tables S1, S2 and S3 for firwood sawdust, olive stone and sewage sludges, respectively). The peak area of a given pyrolysis product obtained by integration in the extracted ion chromatogram of a relevant ion (Tables S1-S3) was normalized to the weight of pyrolyzed biomass sample, an approach similar to that reported in the literature to evaluate the effect of molten salts on the yields of volatiles [11]. The obtained values were abbreviated as WNPA (weight normalized peak area, counts/mg$_{\text{biomass}}$). Peak areas lower than 10 kcounts or severely overlapping peaks were not considered in the calculations. Precision was assessed by triplicate analyses of each biomass (500 °C at 1:5 biomass:salt ratio) by calculating the relative standard deviations (RSD) of the WNPAs. The average RSD values were 15 %, 8 % and 15 % for firwood sawdust, olive stone and sewage sludges, respectively. These values account for the variability within the considered compounds, which is notably higher for smaller areas (< 10 kcounts).

Statistical analysis was conducted using the F-tests ($\alpha = 0.05$) to evaluate the significance of the effect of molten salts on the intensity of the pyrolysis products. A first test assessed the impact of the biomass:salt ratio on peak variances, specifically comparing the calculated WNPA at 1:5 ratio with those at the other tested ratios. A second test evaluated the effect of the molten salts themselves, by comparing the variances of the WNPA when pyrolysis without molten salts was included or excluded from the dataset. Beyond statistical results, the effect of molten salt was also considered significant when its presence caused peaks to disappear.

The effect on single pyrolysis products is reported in Tables S1-S3 for the three feedstocks. The whole data set is available in [36].

3. Results and discussion

3.1. Fir sawdust

Pyrograms obtained from firwood sawdust (FS) at 500 °C, both in the absence and presence of the lowest and highest excess of salts, are presented in Fig. 1 along with the molecular structures of pyrolysis products. These were grouped according to structural similarities and sources. The groups from (hemi)cellulose are oxygenated C2-species (hydroxyacetaldehyde and acetic acid), furanoids (five-membered ring with one oxygen and four carbon atoms with different unsaturation degree), cyclopentenones, pyranones (2- and 4-pyrones), anhydrosugars (levoglucosan and anhydroglucofuranose); the groups from lignin: phenols, catechols (1,2-benzenediols), guaiacols (2-methoxyphenols), dimer.

The total WNPA decreased sharply with the addition of salt, from 0 to 2.5 salt excess (Fig. 2a). In the literature, it was found that the reduction in bio-oil yields gradually decreased with increasing the quantity of molten salt, in salt:biomass ratios from 0.5 to 10 [18]. In our experiments, the WNPA of pyrolysis products was rather similar at 5 and 10 excess, suggesting that under flash conditions of micropyrolysis the influence of different salt proportions could be levelled off.

Specific pyrolysis products that were found to be prone towards the action of carbonate molten salts (1:5 ratio) at 500 °C are presented in Fig. 3.

Levoglucosan, an important pyrolysis product of FS, became negligible in the presence of molten carbonate salts. Similarly, the salt suppressed the formation of anhydroglucofuranose, pyranones and C2-species. Interestingly, cyclopentenones persisted in the pyrolysates with salts. Furanoids decreased mostly because the formation of 2-hydroxymethylene tetrahydrofuran-3-one was suppressed by molten carbonates.

It is evident by looking at the pyrograms of Fig. 1 that the peaks of guaiacols and phenols dominate in the presence of molten carbonates. The WNPA of alkyl guaiacols slightly decreased with the addition of salts, while that of phenols was not severely affected (Fig. 2a). Instead, guaiacols containing oxygenated side chains were decomposed. The aldehyde functionality was particularly susceptible. In fact, vanillin and homovanillin were not detected in the pyrolysates of FS with salts. The disappearance of lignin dimers, represented by (*E*)-4,4'-dihydroxy-3,3'-dimethoxystilbene, was another important consequence of pyrolysis with molten carbonate salts (Fig. 2a).

The effect of temperature was investigated in the 400 °C – 800 °C range at the biomass:salt ratio 1:5. The GC-MS traces reported in Fig. 4 show that important changes in the pattern of pyrolysis products occurred in the 700–800 °C range. The trend of total WNPA presented a maximum at 600 °C, mostly due to the contribution of guaiacols, furanoids, cyclopentenones that peaked almost at this temperature (Fig. 2b). Hydrocarbons (represented by cyclopentadiene and its methylated derivative, benzene, toluene, naphthalene) increased steadily with increasing temperature and became the principal compound family at 800 °C. The increasing contribution of aromatic hydrocarbons in the pyrolysate at high pyrolysis temperature (700–800 °C) was coherent with the aromatisation and defunctionalisation of pyrolysis products of neat biomass catalysed by endogenous alkali metals [9].

Phenols were the second most abundant compound class at 600–800 °C, whereas. catechols, not detected at 400–500 °C, became important pyrolysis products at 700 °C.

3.2. Olive stone

Similarly to FS, pyrograms of olive stone (OS) were featured by thermal degradation products of (hemi)cellulose and lignin (Fig. 5). Obviously, the different type of lignin produced additional peaks due to syringol (2,6-dimethyphenol) units. The presence of molten carbonates provoked the same changes in the pyrolysate composition as those described for FS. Firstly, a decrease in the WNPA, which was more pronounced for cellulose than lignin (see [36]). The salts reduced the presence of levoglucosan, maltol, C2-species (hydroxyacetaldehyde and acetic acid) (Fig. 2c). Instead, the formation of cyclopentenones remained significant as did that of furanoids, with the exception of 2-hydroxymethylene tetrahydrofuran-3-one. The decrease of hydroxyacetaldehyde (Table S2) was not significant, while in the literature a reducing trend of hydroxyacetaldehyde with increasing alkali ions was reported [7].

As observed for FS, the production of phenols did not decrease with carbonate salts, and the pyrolysate continued to be rich in phenols in comparison to other components that were destroyed by carbonates. The concomitant decrease of guaiacols and syringols with increasing pyrolysis temperature indicates that demethoxylation is an important process involved in the enrichment of phenols [37].

The most important effect of salts was observed for methoxyphenols with an oxygenated side chain, in particular the contribution of aldehydes was suppressed (vanillin, homovanillin, syringaldhyde, sinapaldehyde).

Pyrolysis temperature affected the composition of OS pyrolysates in the similar fashion observed for FS, with marked variations in the pattern of pyrolysis products at 700–800 °C (Fig. 6). Total WNPA presented the highest value at 600 °C, as for FS and decreased at higher temperatures due to the reduction of the main chemical families (guaiacols, syringols, cyclopentenones) (Fig. 2d). The WNPA of hydrocarbons increased with increasing temperature and, at 800 °C, became by far the most abundant compound group, as observed for FS. Similarly, the levels of phenols increased, becaming the second most abundant component after hydrocarbons at high pyrolysis temperatures (700–800 °C). Catechols were negligible at 400–500 °C, but were important products at 700–800 °C.

3.3. Sewage sludge

Differing from FS and OS dominated by lignocellulosic components, the pyrograms of sewage sludge (SS) were featured by the peaks evolved from proteins and lipids (Fig. 7 and Table S3). Pyrolysis products specific of proteins included the cyclic dipeptides (diketopiperazines), dominated by Pro-Leu (proline-leucine) and Pro-Pro, and aromatic amines indoles, pyrroles and nitriles. Less specific amines, ethanolamine, pyridine, acetamide and methylpyrrole confirmed the abundance of nitrogen constituents in the SS sample, not exclusively proteinaceous. All the nitrogen-containing compounds were collected into a single compound

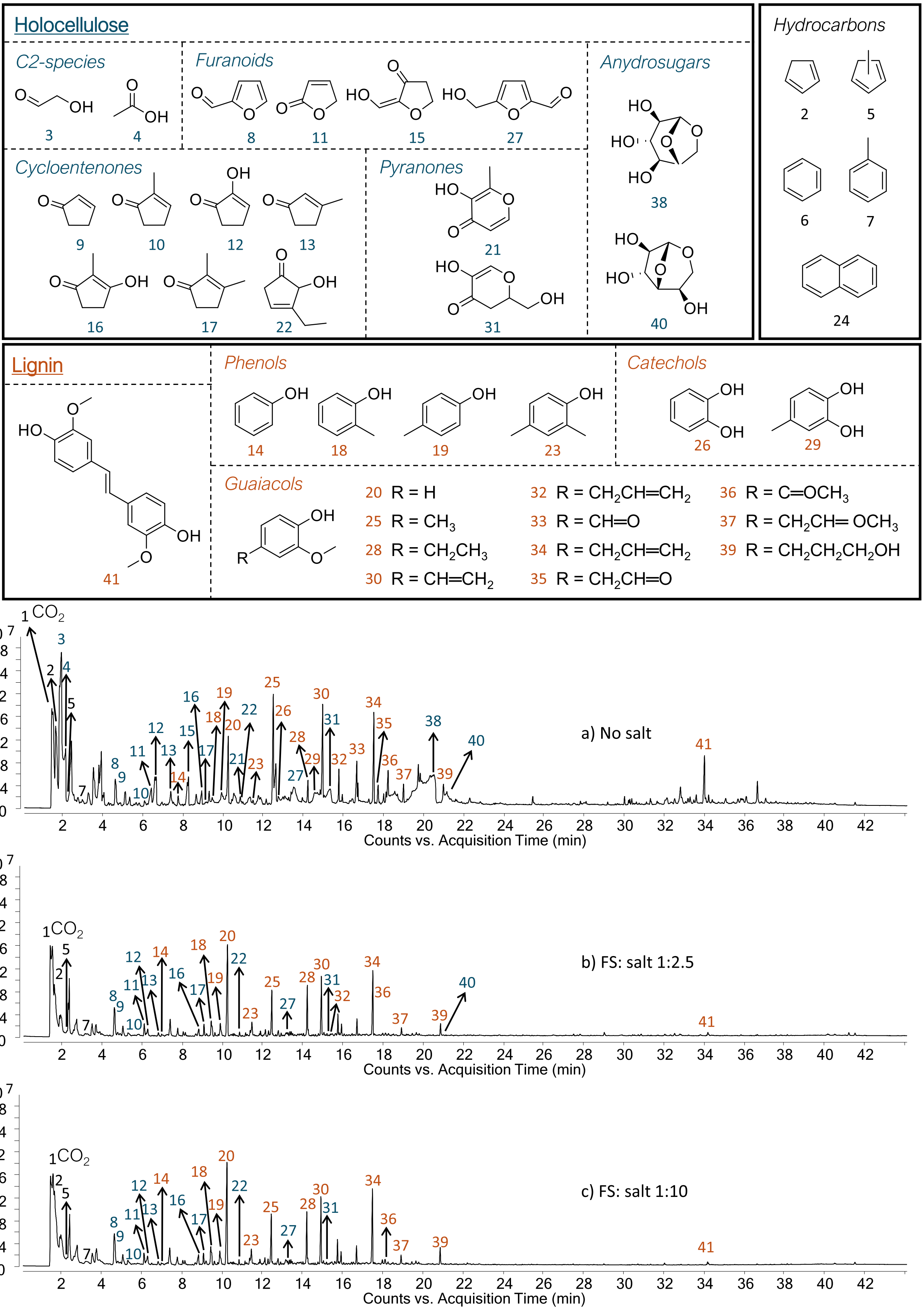

Fig. 1. Py-GC-MS at 500 °C of firwood sawdust without (a) and with (b) lowest and (c) highest amount of molten carbonate salts.

Fig. 2. Py-GC-MS of different biomass with molten LiNaK carbonate salts. Left: weight normalised peak area (WNPA) of compound classes evolved at 500 °C at different salt:biomass ratios (0 no salt, 2.5, 5 and 10) for (a) FS (c) OS and (e) SS. Right: WNPA of compound classes evolved at different pyrolysis temperatures at salt:biomass ratio 5:1 for (b) FS, (d) OS and (f) SS.

family. In the absence of literature data for sewage sludge, the comparison was made with biomass rich in proteinaceous matrices such as algae. Pyrolysis of spirulina with NaK carbonates in a quartz reactor at high temperatures (700–900 °C) showed that most part of nitrogen was distributed in gas (mainly NH_3 and HCN), while a modest fraction ended up in bio-oil [24]. The composition of spirulina-salt bio-oil presented differences (e.g. the absence of long chain alkyl nitriles in our pyrolysates at 700–800 °C) and similarities (such as the presence of pyrroles, pyridine and indoles) with our pyrolysates, probably due the compositional differences between the two matrices. Nonetheless, it was shown that increasing temperatures decreased the contribution of nitriles, while aromatic heterocyclics (pyrrole, pyridine, indole) remained fairly constant from 700 to 800 °C [24]. Phenol and methylphenols can be attributed to the degradation of proteins (e.g. tyrosine) owing to the abundance of nitrogen-containing compounds rather than lignin that produced vinyl guaiacol.

Steroids, representing the lipid fractions, formed a cluster of peaks attributed to C_{27}, C_{28} and C_{29} species without (C_{27}) and with methyl

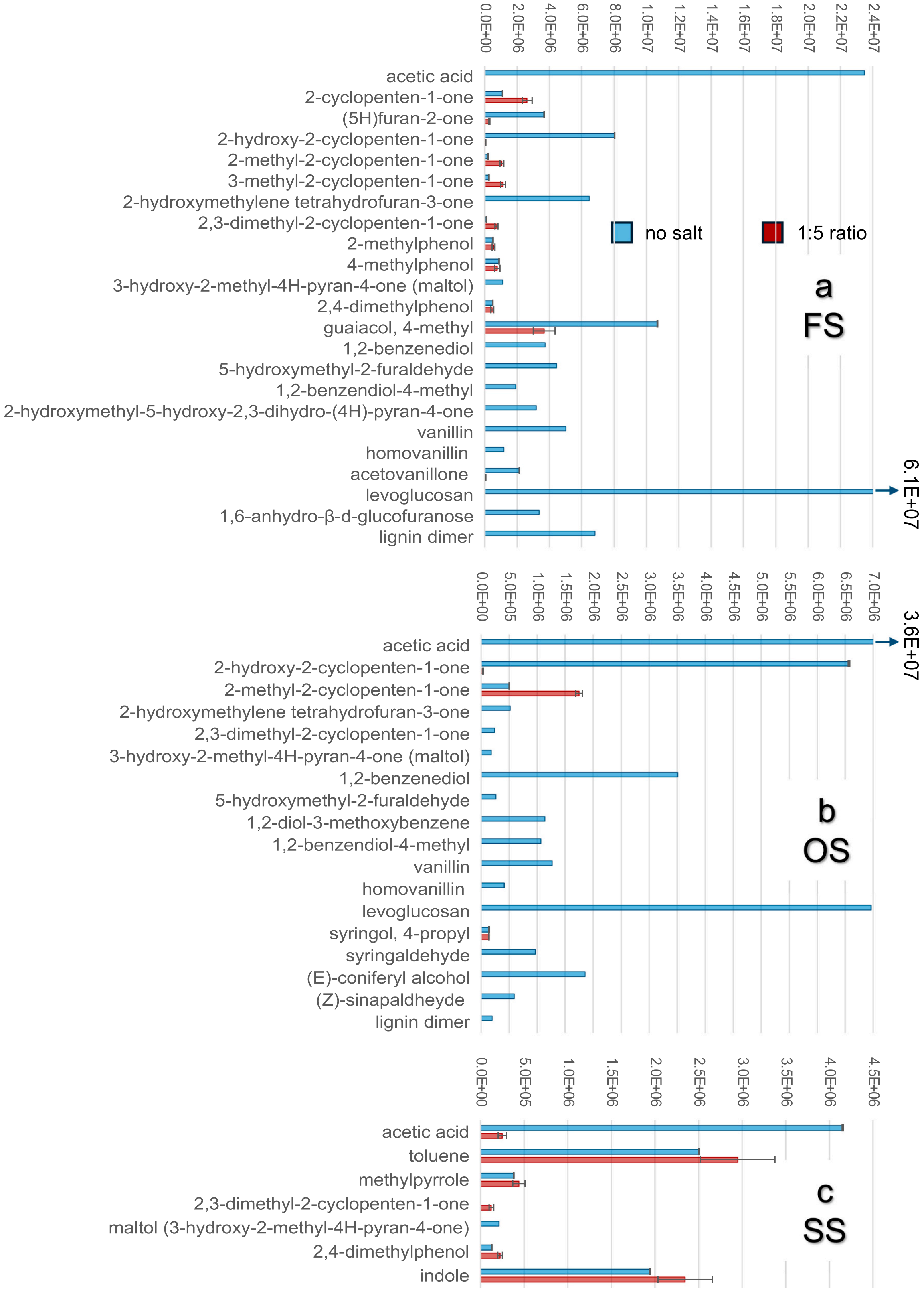

Fig. 3. Weight normalised peak area (WNPA) of pyrolysis products from (a) fir sawdust, (b) olive stone, (c) sewage sludge, significantly affected by the presence of carbonate molten salt. Blue bars without, red bars with molten salt at 1:5 biomass:salt ratio. Pyrolysis temperature 500 °C.

(C_{28}) or ethyl (C_{29}) groups at C-24 (e.g. cholestanes, campestanes and stigmastanes, respectively). The stanols coprostanol, stigmastanol and sitosterol could be tentatively identified by MS, along with their dehydration products (e.g. cholestenes) and oxidated species (e.g. cholestanones) (Table S3). Notably, the steroid pattern was dominated by two compounds that were identified as monothiols containing the HS- in place of HO-group at C-3. The most intense peak was attributed to cholestan-3β-thiol by matching the mass spectrum with literature [38].

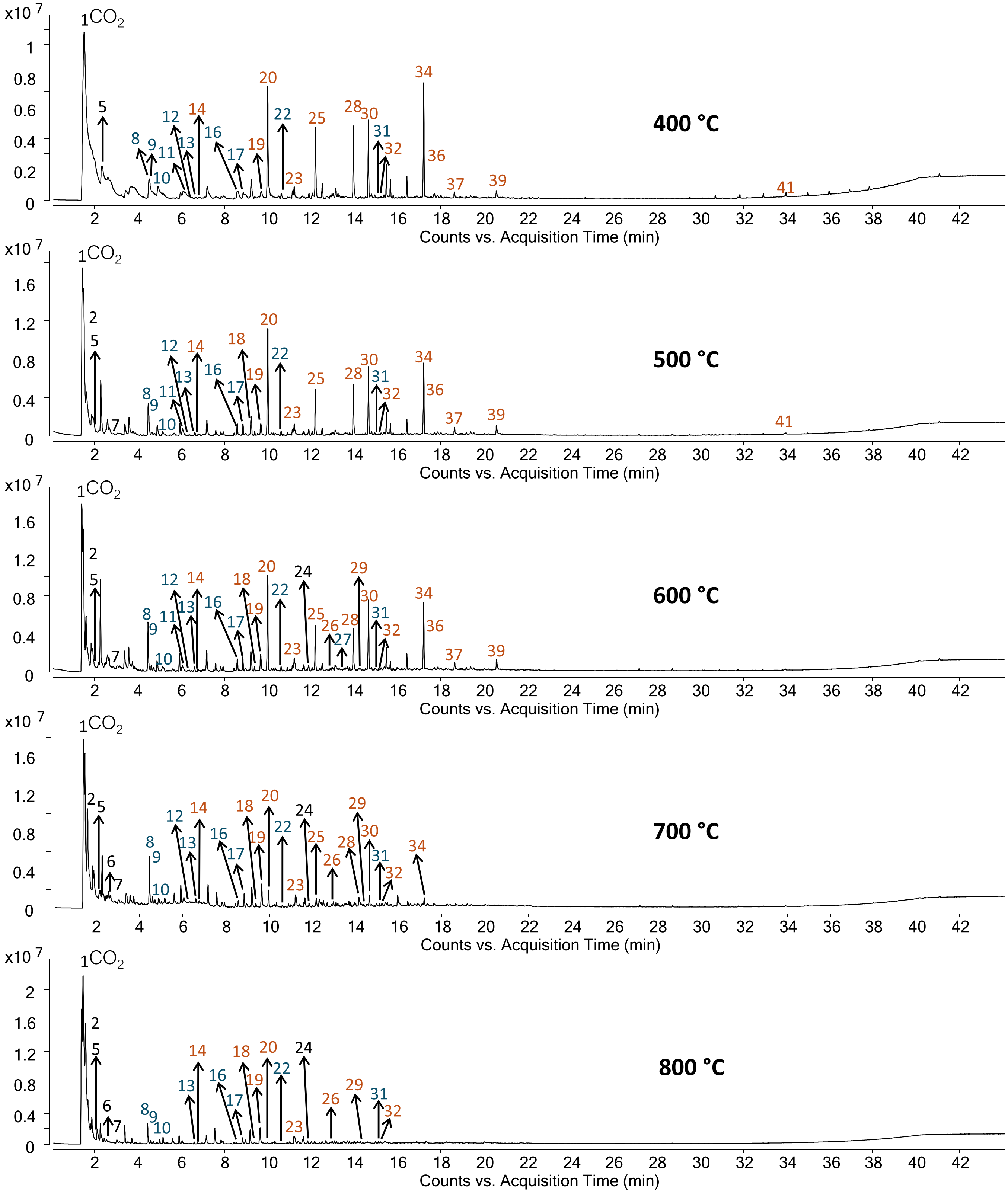

Fig. 4. Py-GC-MS of firwood sawdust with carbonate molten salts (5:1 salt to FS mass ratio) at different pyrolysis temperatures. Peak labels refer to compound numbers in Fig. 1.

Other two sulphurated steroids were tentatively identified by the characteristic fragment ion at *m/z* 249, the molecular ion at *m/z* 404 + 14 and 28 for the C_{28} and C_{29} homologues, respectively [38]. Several steroids reported in Fig. 7 (Table S3) were described by El Fels et al. who studied composting of sewage sludge with palm tree waste by Py-GC-MS [33]. Interestingly, the pattern of steroids was maintained when pyrolysis was conducted in the presence of carbonate molten salts.

Hydrocarbons (cyclopentadienes, benzene, toluene, ethylbenzene,

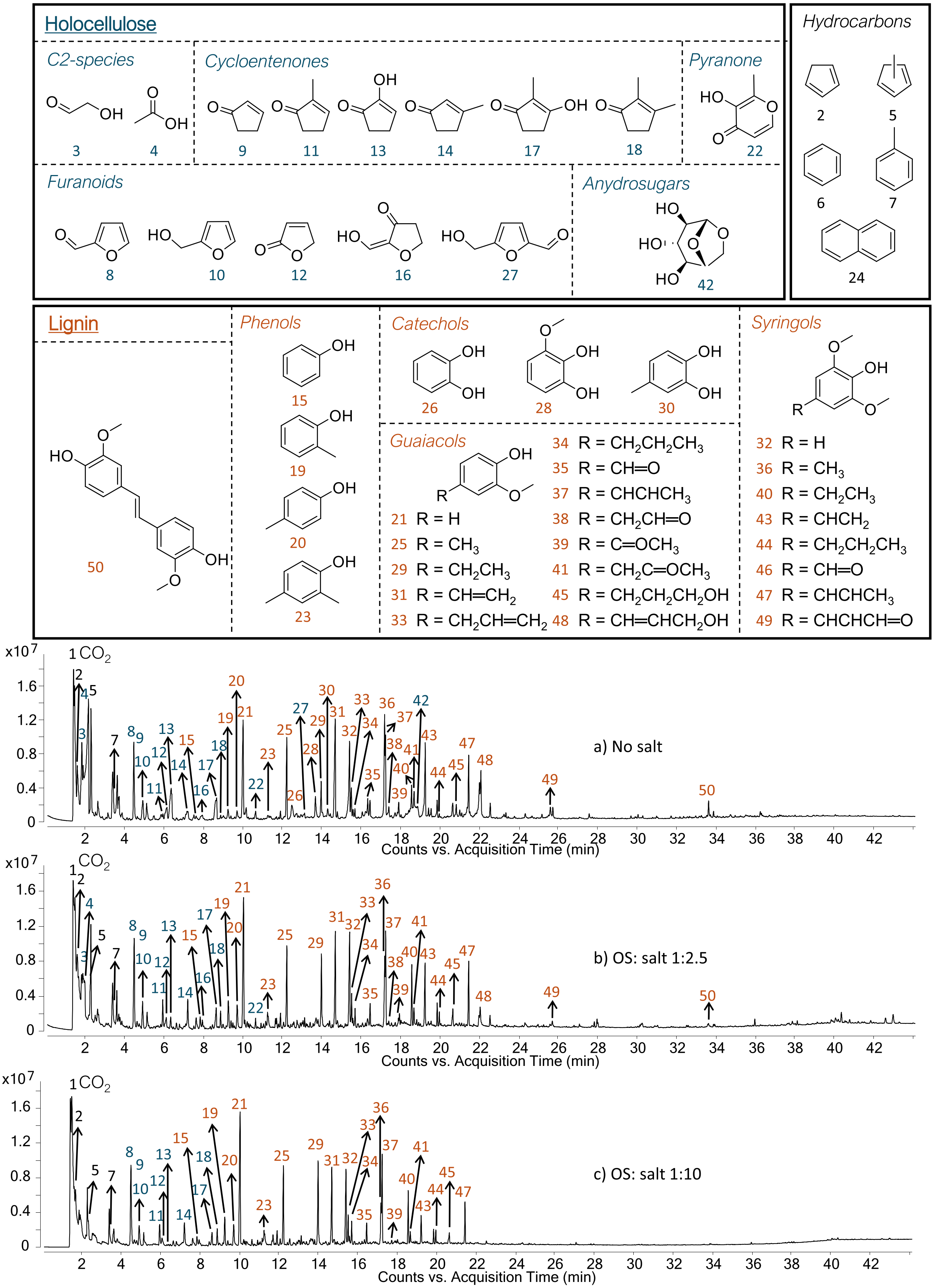

Fig. 5. Py-GC-MS of olive stone without (a) and with (b) lowest and (c) highest amount of molten carbonate salts.

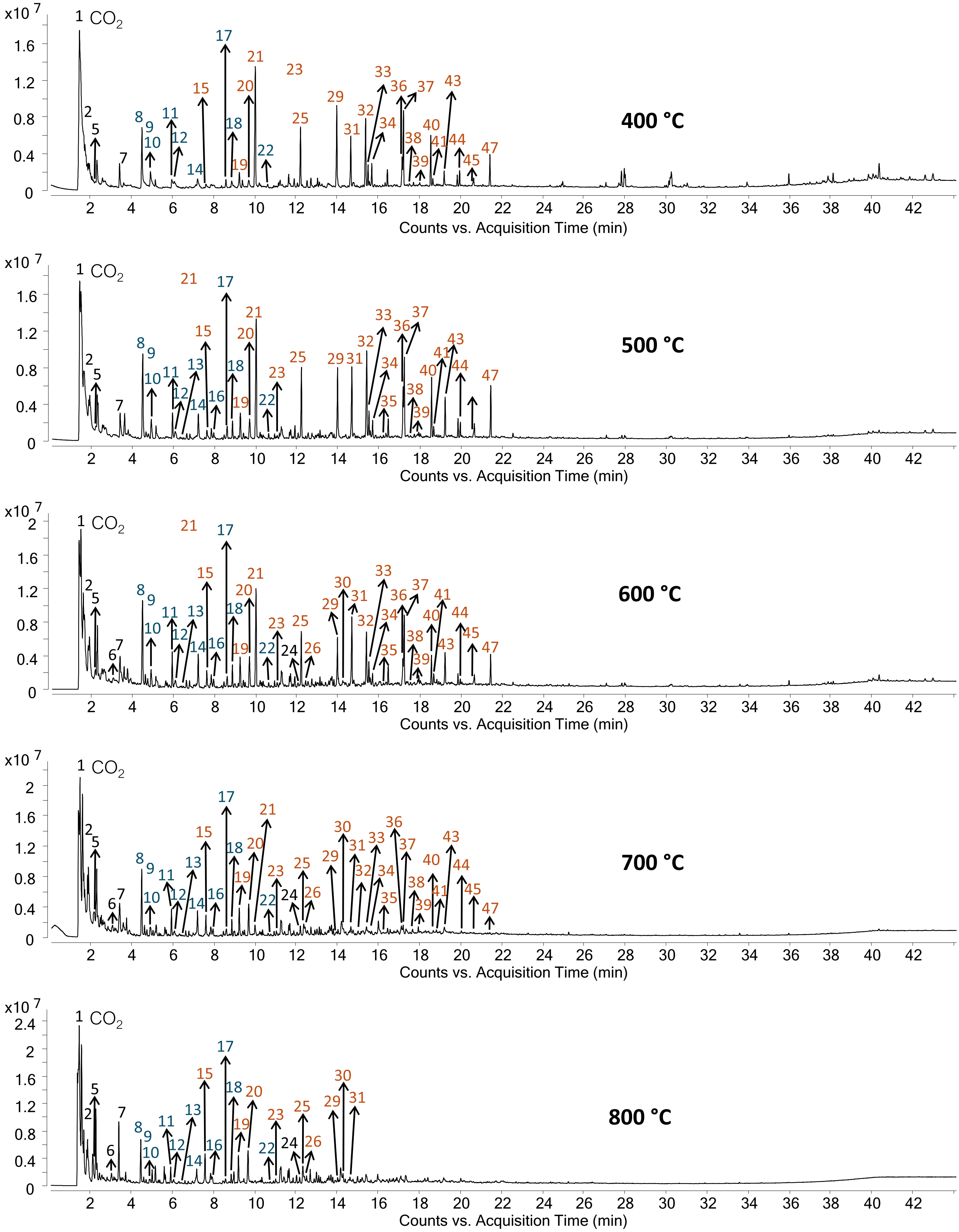

Fig. 6. Py-GC-MS of olive stone with carbonate molten salts (5:1 salt to OS mass ratio) at different pyrolysis temperatures. Peak labels refer to compound numbers in Fig. 5.

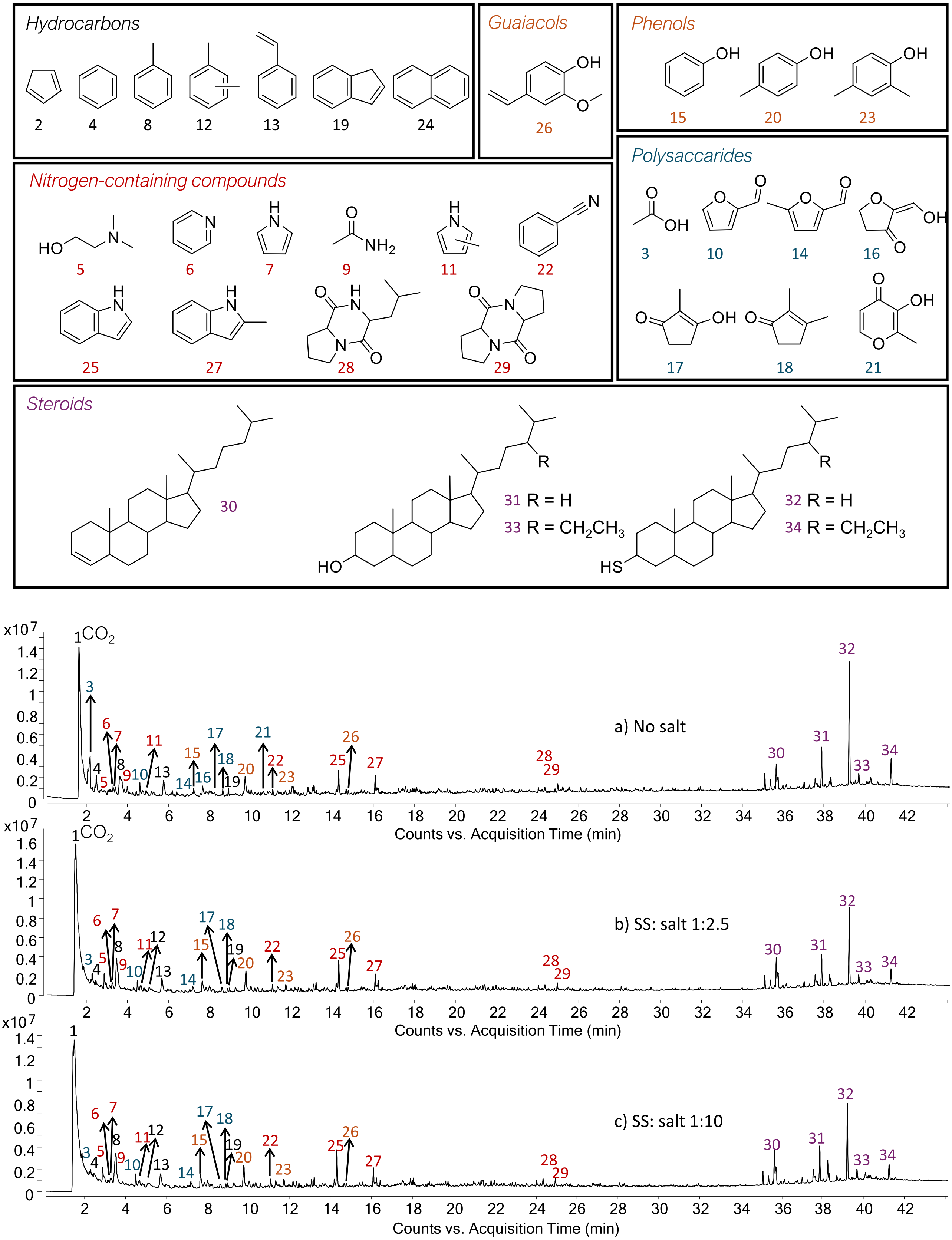

Fig. 7. Py-GC-MS of sewage sludge without (a) and with (b) lowest and (c) highest amount of molten carbonate salts at 500 °C.

styrene, indene) were important pyrolysis products of SS, possibly formed by the thermal degradation of lipids (e.g. unsaturated fatty acids) as well as proteins (e.g. toluene from phenylalanine).

The WNPAs of the chemical families evolved from pyrolysis of SS with and without salts are shown in Fig. 2e. In general, nitrogenated compounds, including cyclic dipeptides Pro-Leu and Pro-Pro, were not significantly altered by the presence and relative amount of molten carbonates. The WNPAs of steroids selected to represent different groups (cholestenes, sterols and thiosterols) did not change significantly without salts and with different salt contents (Table S3).

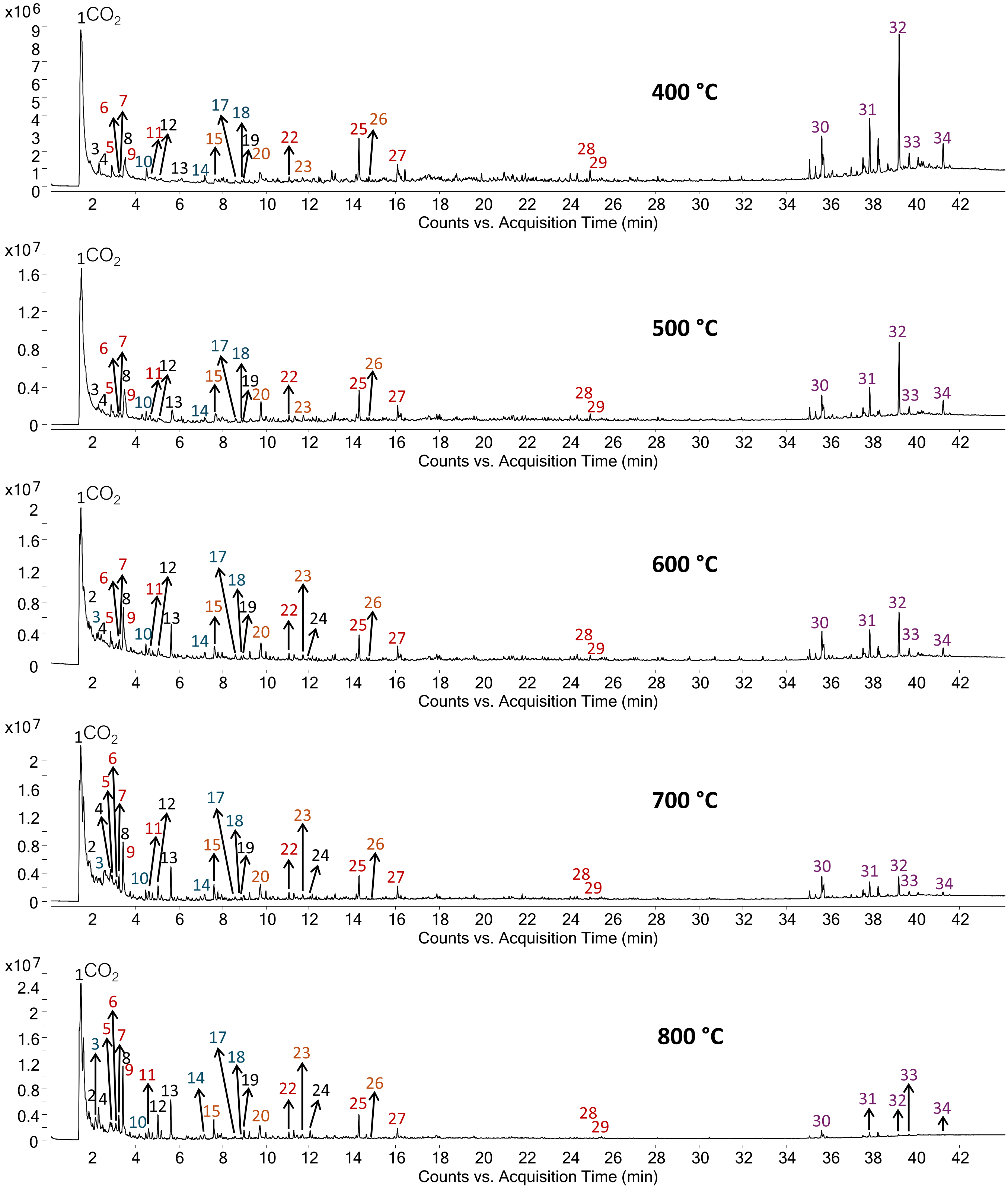

Fig. 8. Py-GC-MS of sewage sludge with carbonate molten salts (5:1 salt to SS mass ratio) at different pyrolysis temperatures. Peak labels refer to compound numbers in Fig. 7.

The presence of salts did not perturb significantly the intensity and the pattern of steroids at 500 °C, indicating that not only the cyclopenta[*a*]phenanthrene carbon skeleton is thermally stable, but the side chain as well. The presence of unusual thiosterans stands out in the steroid pattern, a finding which is in line with literature. In fact, thiosterans were identified by GC-MS in sewage sludge [39] and in environmental samples impacted by sewage effluents by pyrolysis with methylation [40].

As far as polysaccharide markers (furanoids, cyclopentenones and maltol) are concerned, they were grouped into a single family (Fig. 7). These markers decreased in the presence of molten salts due to pyranones diminution, while cyclopentenones remained significant compounds, confirming the data from FS and OS. Acetic acid was still observed with salt:biomass ratios of 2.5 and 5, but not 10.

The qualitative profile of pyrograms of SS with carbonate molten salts did not change substantially with increasing pyrolysis temperature from 400 to 800 °C (Fig. 8). However, total WNPA increased with increasing pyrolysis temperature due to the increased contribution of aromatic hydrocarbons, that constituted the principal compound class at 700–800 °C (Fig. 2f). The WNPAs of nitrogen containing compounds, dominated by aromatic amines, slightly increased with increasing temperature. Instead, cyclic dipeptides (represented by Pro-Pro and Leu-Pro) formed at 400 °C decreased with increasing temperature even though they were detected at high temperatures. Carbohydrate pyrolysis products in the presence of salts were dominated by furans and cyclopentenones, whose WNPAs decreased from 600 °C. The WNPAs of steroids decreased with increasing pyrolysis temperatures, but they featured the high elution time region of pyrogram even at the highest temperature.

Besides being resistant to biodegradation [39], thiosteranes resulted to be rather stable to thermal treatment being detected by Py-GC-MS with the carbonate molten salts even at 800 °C.

3.4. General aspects of carbonate molten salt effect

Overall, Py-GC-MS enabled to ascertain the effect of molten carbonates on the pyrolysate composition evolved by lignocellulosic, proteinaceous and lipidic matrices. The possible reaction mechanism diagrams of biomass pyrolysis in carbonate molten salts have been reported in the literature for lignocellulosic [19] and nitrogen-rich algal [23,24] biomass. In general, thermal degradation processes become relevant starting from about 500 °C (decarboxylation, decarbonylation, dehydrogenation, demethylation, denitrogenation, nitrile decomposition), with increasing importance as temperature increases.

The most important effects of molten carbonates were observed for lignocellulosic biomass, that produced a lower amount of several pyrolysis products from lignin, hemicellulose, cellulose (Figs. 3a and 3b). This finding is in line with the lower yields of bio-oil reported for pyrolysis of lignocellulosic biomass with molten LiNaK carbonates with bench scale reactors [10,18,19]. On the contrary, several pyrolysis products of sewage sludge persisted, or even increased, in the presence carbonates (Fig. 3c). The molten salt effect for different pyrolysis products is summarised in the following paragraphs.

3.4.1. Acetic acid and furanoids

Furanoids were not significantly altered by salts, with the exception of hydroxymethylfuraldehyde and 2-hydroxymethylene tetrahydrofuran-3-one. This latter compound, a marker of hemicellulose [41], after having previously been identified as 4-hydroxy-5,6-dihydro-2H-pyran-2-one from hemicellulose [42], was identified as 2-hydroxymethylene tetrahydrofuran-3-one by a synthetic approach [43]. Acetic acid, another pyrolysis product of hemicellulose, was suppressed by carbonate molten salts, in accordance with the analysis of cotton stalk bio-oil collected from quartz reactors [10]. Contrarily to carbonates, acetic acid was retained in the presence of molten chloride salts [11] suggesting that carbonate ion plays a role in the suppression of acetic acid (e.g. by ketonization [19]).

3.4.2. Pyranones and anhydrosugars

Molten carbonates were detrimental to the formation of levoglucosan and anhydroglucofuranose (Figs. 3a and 3b). It is known that Na^+ and K^+ ions degrade levoglucosan and favour the formation of C2-C3 pyrolysis products, such as hydroxyacetaldehyde (glycolaldehyde) [5] or acetic acid [4,7]. These C2 compounds were further degraded in the presence of molten carbonates. Similarly to anhydrosugars, the formation of pyranones (maltol and 2-hydroxymethyl-5-hydroxy-2,3-dihydro-(4 H)-pyran-4-one) was inhibited by molten carbonates. The reduction of anhydrosugars which are soluble in water, as well as other hydrophilic components, such as acetic acid, is expected to provide a bio-oil with improved quality as a fuel [10], but inadequate characteristics for hybrid thermochemical-biological processes which require fermentable compounds [44].

3.4.3. Cyclopentenones

Contrarily to other pyrolysis products of cellulose, the production of cyclopentenones increased for all biomass types (Fig. 3a-c). Moreover, these compounds remained relevant products of the pyrolysates of biomass in the presence of carbonates under different conditions of salt ratio and pyrolysis temperature (Fig. 2). This outcome is in accordance with studies on bench scale reactors [18,19]. Pentacyclic ketones are pyrolysis products of polysaccharides, identified by GC-MS in fresh biomass, and persisted as relevant constituents in the hydrous pyrolysates of geological fossil organic matter, suggesting a notable resistance of these compounds against the catalytic action of minerals [31]. It was reported that K^+ ions promoted the formation of several cyclopentenones from the pyrolysis of levoglucosan [4]. Cyclopentenones are probably decarbonylated at high pyrolysis temperatures [19], rising the pool of aromatic hydrocarbons observed at 700–800 °C.

3.4.4. Phenols and methoxyphenols

Phenols were not strongly influenced by molten carbonates. This observation is concordant with the GC-MS analyses of bio-oil obtained pyrolysis of molten carbonates of lignin [25], digestate rich in lignin [21], lignocellulosic biomass [18,19]. Althought small, significant changes were observed only for methyl phenol (Fig. 3a) and 2,4-dimethylphenol (Fig. 3c).

The action of molten carbonates was relevant for methoxyphenols bearing side chain with oxygenated groups, especially aldehydes, that were not evolved in the presence of molten carbonates. Dimers, represented by 4,4'-dihydroxy-3,3'-dimethoxystilbene, were not revealed in the presence of salts.

3.4.5. Benzenediols

Likewise molten chlorides pyrolyzed with lignin at 350 °C [11], benzediols were not detected with carbonates at low pyrolysis temperatures (400 – 500 °C). However, with molten carbonate salts, benzenediols were formed at higher pyrolysis temperatures (600–800 °C), probably from the demethylation of methoxyphenols.

3.4.6. Amines

Interestingly, the formation of nitrogen containing compounds was not altered by the presence of molten carbonates (Table S3),with the exception of methylpyrrole and indole that increased (Fig. 3c). This finding appears to contrast the results by Xu et al. who reported lower yields of bio-oil associated to the removal of nitrogen, including aromatic species, due to carbonate molten salt [23]. Similarly, Wei et al. [21] on seaweed pyrolysis in ternary molten carbonates (Li_2CO_3-Na_2CO_3-K_2CO_3), declared that the nitrogen-containing compounds in bio-oil were reduced by nearly half. These discrepancies could be due to the different chemical nature of the proteinaceous matrix or different pyrolysis processes that need further studies to be confirmed.

In general, the influence of carbonate molten salts on the pyrolysis of lignocellulose was coherent with the combined actions of alkali metal ions and with the alkaline nature of CO_3^{-2} [8]. In fact, the changes of product distribution induced by $(NaK)_2CO_3$ were stronger in comparison to those observed by (NaK)Cl and $(NaK)_2SO_4$ (cellulose and bamboo, 550 °C, up to 20 % salt) [8]. This outcome indicates that the chemical effects of alkali carbonate molten salts are mostly driven by the chemical characteristics of the individual carbonates. The molten state strengthens these effects owing to the physical behaviour of the liquid phase. The viscous liquid phase acts as a diffusion barrier that increases the residence time of the entrapped volatiles, promoting secondary reactions catalysed by alkali ions towards the formation of gas at the expenses of bio-oil [19]. The diminution of evolved products from lignocellulosic biomass was explained by inhibited devolatilisation due to diffusion barrier of the molten salt, embedding biomass particles that increased the residence time of vapors favouring secondary reactions [11]. These reactions (cracking, homolytic cleavage, aromatization, dehydration etc.) are catalysed by alkali metal ions promoting the formation of char and non-condensable gases at the expenses of vapours condensable into bio-oil [4–9].

4. Conclusions

Py-GC-MS was confirmed to be a useful technique to provide preliminary information about the effect of molten salts on the chemical composition of bio-oil obtainable with bench scale pyrolysis reactors. Pyrolysis with molten carbonate salts could decrease the quality of bio-oil for hybrid thermochemical-biological treatments (e.g. biogas production) due to the reduction of water soluble components. Improvements of bio-oil can be expected as fuel for the reduction of reactive (e.g. aldehydes), corrosive (e.g. acetic acid) and hydrophilic components (e.g. hydroxypyranes). However, the persistence of amines is a critical aspect of bio-oil from sewage sludge. High pyrolysis temperatures (> 700 °C) are required to obtain a pyrolysate enriched in aromatic hydrocarbons and simple phenols.

CRediT authorship contribution statement

Fabbri Daniele: Writing – review & editing, Writing – original draft, Funding acquisition, Conceptualization. **Yang Haiping:** Conceptualization. **Wang Shurong:** Funding acquisition, Conceptualization. **Torri Cristian:** Conceptualization. **Facchin Andrea:** Software, Methodology. **Ahmadi Elahe:** Writing – original draft, Methodology, Investigation, Formal analysis. **Coralli Irene:** Visualization, Formal analysis, Data curation. **Fantozzi Francesco:** Funding acquisition. **Rombolà Alessandro G.:** Methodology. **Zangheri Martina:** Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jaap.2025.107144.

Data Availability

Data will become available in a redipository platform AMS Acta University of Bologna

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