Product yield, quality and energy in the hydrolysis of urban bio-waste compost from laboratory-scale runs

(Article begins on next page)

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Products yield and quality and energy involved in the hydrolysis of urban bio-waste compost

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ABSTRACT

The valorization of bio-waste is pursued to cope with the increasing amount of waste due to human consumption habit, and to find alternative renewable feedstock to fossils for manufacturing fuel and chemicals. Currently, bio-waste is processed by fermentation and thermochemical technologies, producing biofuel, compost and small platform molecules. Commercial low temperature chemical processes to valorize the bio-waste lignin fractions as feedstock of value added chemicals are missing. The present work addresses this technology gap showing that the low temperature hydrolysis of municipal bio-waste compost is a safe ecofriendly cost effective process to convert the compost' lignin-like material to value added speciality chemicals. It is reported that the process yields soluble biopolymers (SBO) at 30 to 70 % yield upon increasing temperature from 60 to 150 °C. The 150 °C SBO exhibit the best surfactant properties, prospecting their multipurpose use. The reaction yield is limited by non-hydrolysable lignin-like matter present in the pristine compost. Energy changes occur due to endothermic and exothermic reaction during hydrolysis at different temperature. The process allows recycling most of process water and reagent, and saving reagents, water and process energy. No secondary treatment of process effluent is necessary. The data prospects the feasible production of SBO at commercial level through low temperature hydrolysis of compost or biomass from different sources.

Keywords: Lignin, compost, bio-waste, hydrolysis, energy consumption, bio-based products

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Abbreviations
Soluble bio-based substances (SBO)
Insoluble residue (IR)
Municipal Bio-Waste (MBW)
MBW compost (CVD)
Weight average molecular weight (M_W)
Number average molecular weight (M_N)

1.   Introduction

Bio-waste processing is necessary to cope with the increasing bio-waste amount produced by the increasing population and consumption habit. Moreover, bio-waste is a potential feedstock to produce speciality chemicals and commodities, which may replace products from fossil sources. The prime objective is to assure a clean sustainable environment to live in. This implies developing clean and/or eco-friendly bio-waste processes and derived products. Processes should use green solvents and chemicals, and produce minimum secondary waste requiring disposal. This work addresses the following issues.

1.1. Technology and feedstock

In principle, all bio wastes are potential feedstock for producing bio-based chemicals. In practice, this implies coping with two main criticalities. Compared to fossils, bio wastes contain relatively too much water. The latter are spread over large areas. Moreover, processes developed for bio-waste are not necessarily clean and economically sustainable. Among all solid bio-waste types from urban, agriculture and agro-industrial source, fermented municipal bio-waste is the most exploitable feedstock (Montoneri et al., 2011).

Municipal bio-waste (MBW) contains unsorted food waste and gardening residues (Montoneri, 2017). Food waste comes from home and restaurant kitchen wastes, and unsold vegetables of food stores and supermarkets. The concentration of wastes in urban areas has allowed collecting natural bioorganic matter in well-confined spaces, with transportation costs covered by the taxpayer. In addition, anaerobic and/or aerobic fermentation of this bio-waste allows reducing the content of water and obtaining materials with higher concentration of organic matter. By these features, urban bio-wastes are defined negative cost feedstock (Sheldon Coulson, 2011). Nevertheless, not all processes for attaining these features are clean or require no secondary treatment of the products to be environmentally acceptable. A typical example is the anaerobic fermentation of bio-waste. Municipal bio-waste treatment plants (Montoneri et al., 2011) perform the anaerobic digestion of the organic fraction of urban bio-waste, alone or followed by the aerobic fermentation of the digestate mixed with gardening residues. The anaerobic fermentation yields biogas and digestate. Both biogas and residual digestate matter are useful products. Unfortunately, the latter requires a secondary treatment (Francavilla et al., 2016). This is necessary because the bio-waste fermentation produces also ammonia, which has important negative environmental impact. Recently, soluble biopolymers (SBO) obtained by alkaline hydrolysis of MBW composted, added at 0.05-2.0 % concentration in the fermentation slurry, have been shown to reduce the ammonia content in the anaerobic fermentation digestate (Fracavilla et al., 2016). Moreover, SBO have been demonstrated suitable for use in several other fields such as chemical industry, agriculture and animal husbandry (Montoneri, 2017). These findings prospect a virtuous bio-waste cycle to produce biogas without ammonia and speciality bio-based chemicals. A MBW treatment plant might be turned into a bio refinery (Montoneri et al., 2011). The plant would integrate the available conventional fermentation facilities with the new compost hydrolysis facility, and produce biofuel and SBO for use as additive in the in-house anaerobic fermentation reactors, and for sale to multiple potential users. Thus, there are sound reasons for developing a clean sustainable bio-waste hydrolysis process.

1.2. Lignin valorization

Composted MBW contains lignin-like material. This is the insoluble residue of polysaccharide, protein, fats and lignin proximates in food and gardening organic matter that survives the fermentation process (Rosso et al., 2015). Thus, hydrolysis of MBW compost allows addressing the broader issue of valorising lignin as source of value added chemicals.

The removal and conversion of lignin to value added products (Montoneri et al., 2016) is a critical point and a major issue for valorising biomass as source of renewable fuels and chemicals. This is because lignin inhibits fermentation microorganisms, and is an insoluble recalcitrant material withstanding biochemical and chemical treatment. Lignin is the second most abundant organic component in the vegetable world. The emerging biomass refinery industry will inevitably generate enormous amounts of lignin. Development of selective bio refinery lignin-to-bioproducts processes will play a pivotal role in significantly improving the economic feasibility and sustainability of biofuel production from renewable biomass.

Current biomass treatment technology (Montoneri et al., 2016), mainly focused on the production of biofuel by fermentation, such as biogas and bioethanol, adopts a variety of biomass pretreatment methods to remove lignin from the fermentable fraction and/or processes the residual lignin fraction by combustion, pyrolysis, hydrocracking, or aerobic fermentation. These processes, respectively, convert the chemical energy to thermal and electric energy, produce hydrocarbons and other platform chemicals, and compost that is used for landscaping and/or soil fertilization. Yet, the biowaste lignin fraction has further potential, which can be exploited by low temperature chemical technology.

Previous work has reported the acid and alkaline hydrolysis of various lignocellulosic feedstock. The alkaline process causes less sugar degradation. It removes uronic acids and acetyl groups from polysaccharides and increases the accessibility for enzymes for further hydrolysis. It cleaves the intermolecular ester bonds between the lignin and polysaccharide proximates of the feedstock. The solubilisation of lignin matter from different sources by hydrolysis under alkaline conditions has been reported by hydrothermal treatment at 200-400 °C of wheat (Janker-Obermeier et al., 2012) and triticale straw (Monteil-Rivera et al., 2012), walnut shell (Liu et al., 20116), sawdust and rice husk (Karagoz et al., 2005), rice bran (Pourali et al., 2010), and several other biomass residues (Zhang et al., 2008). Main products reported under these conditions are small phenolic molecules. The valorisation of lignin as source of value added water soluble biomacromolecules has been reported for the first time by Montoneri et al. (2011). These have been obtained by hydrolysis of composted MBW at 60 °C and pH 13. The constraints of the hydrolysis reactions to convert the recalcitrant lignin fraction in biomass to useable bio-based product will be discussed in further details in section 3, comparing with the results obtained in the present work with those reported in the above cited references.

1.3. Feedstock and products chemical composition

Assessing the chemical nature of the compost and hydrolysis products is quite difficult. The compost contains the insoluble lignin-like matter surviving the fermentation process. The SBO are mixes of polymeric molecules containing organic C and N distributed over a variety of aliphatic and aromatic C moieties substituted by acid and basic functional groups, which are bonded to several mineral elements such as Na, K, Ca, Mg, Al and Fe (Rosso et al., 2015). These molecules save the memories of the protein, fats, polysaccharide and lignin proximate in the pristine bio-waste. They are associated to the products multipurpose properties as surfactants, agents for sequestering or carrying small molecules and mineral ions in

solution, photosensitizers and reactive biopolymers. Under these circumstances, the SBO chemical composition cannot be assessed as well as for synthetic simple molecules or polymers obtained from fossil feedstock. Montoneri et al. (2011) have developed an analytical protocol to characterize biowaste matter from different sources. It comprises 13C NMR spectroscopy, potentiometric titration, SEC-MALS molecular weight determination, and C and N elemental analysis. The resulting analytical data allow evidencing important composition differences among feedstock from different sources and among products obtained by hydrolysis at 60 °C. The products chemical differences have been confirmed to affect significantly products' properties. The second major difference of the present work, compared to the previous work (Rosso et al., 2015), is the application of the above analytical protocol to assess the effect of temperature on the products chemical nature.

The hydrolysis of MBW compost to produce SBO has been reported first at 60 °C. The intent was to produce and characterize products chemical composition and performance in a variety of applications (Montoneri et al., 2011). Following the assessment of the products value, Rosso et al. (2015) carried a preliminary investigation of the main process parameters. The hydrolysis of a compost (CVD), obtained from municipal food waste and gardening residues, was investigated as a function of several reaction parameters. Althoug water is the most desirable desirable green solvent, excess process water may strongly impact the process energy consumption for its removal and recovery of the SBO. The liquid-solid contact time, and the process temperature, strongly affect the process productivity, equipment capital cost, and the energy consumption. The results of Rosso et al. (2015) investigation demonstrated that the minimum and optimum added water/compost feed ratio is 4 and that the optimum pH of the feed slurry is 13. No definite effect was assessed by the liquid/solid ratio above 4. The SBO yield was found to increase upon increasing the reaction temperature and the solid/liquid contact time. The temperature effect was six fold higher than that of the contact time. The results obtained from microwave-assisted runs demonstrated the optimum liquid/solid contact being 60 seconds, and no effect on products yield upon increasing it above 60 seconds. The collected data did not allow assessing whether increasing product yield upon increasing temperature allowed maintaining the chemical composition and properties of the products obtained at 60 °C. This remained one main weak point of the previous study (Rosso et al., 2015) and a most important issue to be addressed in the present study.

1.4. Process energy

Characterization of the energy involved in the process is another important issue, which Rosso et al. (2015) did not address. Determination of process energy consumption at laboratory level does not always reflect the situation in real operational conditions at commercial production level. Yet, understanding the energy involved in chemical reactions is of crucial importance in the chemical industry (Bitesize, 2014). This is not only for the effects on process cost, but also for safety reasons (The Open University, 2017). Exhotermic reactions, if not properly controlled, can cause abrupt pressure rise and explosion. Accidents during hydrolysis involving well known organic compounds and alkali have been reported (Gustin, 2011). The risk of energy changes is particularly relevant in the biowaste compost hydrolysis. In this case, several different unknown molecules and bonds participate in the reaction. Unpredicted exothermic reactions are more likely than in synthetic chemistry where reagents are known chemical compounds. The temperature rise due to unexpected exothermic reactions should be more safely studied at lab level, rather than having to face it during industrial operation risking human lives. To this end, microwave heating is a valuable laboratory tool. In the present work, to measure the

energy involved in the chemical interactions and reactions between feedstock and reagents, it was found convenient to carry the CVD reaction in the 60-150 °C range using a monomodal microwave reactor (see section 2).

1.5. Innovation

Compared to the previous work (see sections 1.2 thorugh 1.4), the present work presents new aspects. One is represented by the municipal biowaste compost as lignin-like feedstock. The hydrolysis of lignin-like material contained in compost is a novelty, except for the previous studies by Rosso et al. (2015). These authors indicated the effects of the main process parameters such as the temperature, liquid-solid contact time and relative ratios, and pH, and the effects of the nature of the sourcing materials on the products' chemical composition at low reaction temperature. However, Rosso et al. (2015) did not assess the effect of the process temperature on the products' quality and performance. By comparison, the present study confirms previous effects of the process temperature in the 60-150 °C range on products yield and provides new data on the products chemical composition and performance as a function of the reaction temperature. This is of primary importance for scaling up process and products to industrial production and commercial level. The approach taken in the present work may not be innovative from the basic science point of view. Yet, the collected data is highly important because it demonstrates that both process and products can be scaled up to industrial and commercial level in sustainable fashion. Sustainability is the main issue connected to the valorization of biowastes as feedstock for the production of bio-based chemicals. The authors are not aware of similar studies performed on MBW composts. Moreover, it will be shown that, compared to previous work on lignocellulosic materials from different sources (see section 1.2), the results of the present work allow understanding more the reason of the difficulties and limitations presented in studies aiming to the valorization of lignin as feedstock for the production of value added chemicals.

It should be clear that the here in after reported experimental work is not meant to demonstrate the sustainability of microwave-assisted versus conventional hydrolysis. In this work microwave has been used only as a mean to obtain rapidly data on the relation of process parameters and products yield, chemical composition and properties, and on the involved process energy. The authors are aware that energy consumption analysis included in the manuscript merely accounts the energy consumption from lab equipment. This needs to be validated in real commercial-scale operational conditions. Yet, the results obtained from the used lab microwave reactor have allowed assessing the occurrence of energy changes due to endothermic and exothermic reaction during the compost hydrolysis at different temperature. This is a further innovation. The work cited in section 1.2 identifies some of the products obtained in the hydrolysis of lignin, but provides no process energy data.

2.   Methods

The CVD was available from previous work (Rosso et al, 2015). It was made from the anaerobic digestate of MBW food wasteand from gardening residues. These were mixed in 2/1 w/w ratio, respectively, and composted for 110 days. The CVD hydrolysis was carried out in a monomodal microwave reactor (300 °C, 30 bar), Monowave 300 (Anton Paar, GmbH, Graz, Austria). The reactor is equipped with built-in infrared sensor for temperature measurement, integrated hydraulic pressure sensor for monitoring the reaction progress, . and accessories for automatic

recording of temperature, pressure and power throughout the reaction time. The total employed power is measured through integration of the recorded power over the reaction time by software provided by the manufacturer. In the reactor, only one reaction vessel can be irradiated at a time, as the sample must be placed at the antinodes of the field, where the intensity of microwave radiation is the highest. In this way, the rate of heating is very high, and a heat transfer medium is not necessary. Nitrogen provides both the counter pressure and cooling. Two CVD grams were suspended in 8 mL of 1 M KOH solution (1 M) in a 20 mL borosilicate glass vial, to obtain liquid/solid ratio = 4. The experiments were performed under 470 rpm agitation, at 60, 100 and 150 °C, and at a constant power (50W and 100 W). The same experiments were performed with the separate components (see section 3.2).

The CVD hydrolysis produced the SBO and an insoluble residue (IR). The hydrolysate slurry was centrifuged. The supernatant liquid phase and the settled solid phase were dried at 50 °C to obtain the solid SBO and IR products, respectively. The products were analyzed for ash, and elemental organic C and N, and inorganic C content as previously reported (Rosso et al., 2015). Table 1 reports the SBO and IR compositional data, as a function of reaction temperature. Table 2 reports the products yield data. This data, referred to the starting CVD and added KOH dry matter, was calculated based on the recovered SBO and IR products' weights, and on Table 1 data according to the following equations:

$$DM_p \% = 100\ w_p/(w_{cvd} + w_k)\ (1),$$
$$Inorg\ C_p \% = 100\ (w_p\ C_{inp} - w_{cvd}\ C_{in})/(w_{cvd}\ C_{in})\ (2),$$
$$Org\ C_p \% = 100\ w_p\ C_{orgp}/(w_{cvd}\ C_{org})\ (3),$$
$$N_p \% = 100\ w_p\ N_p/(w_{cvd}\ N_{cvd}\ (4),$$

where the subscripts stand p for the SBO or IR product, CVD for pristine CVD, k for KOH, w = weight, yield % are DM_p % for dry matter, Inorg C_p % for inorganic C, Org C_p % for organic C %, Np % for N, C_{inp} and C_{orgp} = inorganic and organic C concentration % in product, respectively, C_{in} and C_{org} = inorganic and organic C concentration % in pristine CVD, respectively, N_p and N_{cvd} = nitrogen concentration % in product and pristine CVD, respectively. Inorganic and organic C, and N concentrations in products and pristine CVD were determined as previously reported (Montoneri et al., 2016). To characterize the SBO chemical composition as a function of reaction temperature, the raw SBO was dissolved in water at 2 % w/w dry matter concentration, and filtered through a polysulphone 5 kDa cut off membrane to remove excess KOH and low molecular weight organic matter with the permeate. The retentate was dried at 50 °C and further analyzed by 13C NMR spectroscopy, potentiometric titration, SEC-MALS molecular weight determination, and C and N elemental analysis, and for surface activity using a K100 Tensiometer from Kruss, according to previously reported methods (Montoneri et al., 2016).

Data comparison for assessing statistically significant differences was performed by one-way ANOVA (P < 0.05) followed by the Tukey's test for multiple comparison procedures. Data fitting was performed using OriginPro 8 software.

3.   Results and discussion

Previous work demonstrated that SBO have much higher and wider potential marketability than IR (Montoneri et al., 2011). Thus, further development of the hydrolysis process aimed to enhance the conversion of the pristine CVD to SBO.

Table 1 shows that, at all temperatures, SBO contain more organic C and N than IR. Second, the C/N ratio in IR steadily increases upon increasing temperature. It shows over 2-fold increase from about 13 at 60 °C to 32 at 150 °C. By comparison, the C/N ratio in SBO does not show a definite relation temperature. It runs randomly from 7.8 to 8.9.

Table 2 shows that the starting CVD and added KOH dry matter is well recovered with SBO and IR. The same does not occur for total organic C and N. Total N recovery is relatively lower than for organic C. The trends of the recovery values reproduce the trends for the products analytical values in Table 1. The SBO dry matter, C and N yield increase upon increasing temperature. The IR yields show opposite trend.

Table 1 and 2 report also the results of the ANOVA analysis, assessing the statistical significance of the effect of the reaction temperature on each indicator of product chemical composition and yield. The most significant effects result for the SBO organic C and N content in Table 1 and for the SBO dry matter, organic C and N yield in Table 2. The yield of SBO organic C (Y_C) and N (Y_N) values versus temperature (T) fit the equation $Y_{C \, or \, N} = a + b \, T$ (5). In equation 5, the values for the intercept (a), slope (b), standard errors, and correlation coefficient (R) are: for Y_C, a = 12.2 ± 3.4, b = 0.38 ± 0.03, R = 0.99; for Y_N, a = 15.4 ± 12.4, b = 0.34 ± 0.11, R = 0.90. In each regression three data points, each point being the average of triplicate runs, are involved. The high correlation coefficients show that the effect of temperature is statistically highly significant.

The data in Table 2 shows that the reaction produces about 7 % total inorganic C, in excess of the inorganic C content in the pristine CVD. The excess inorganic C stems from mineralization of pristine CVD organic C during hydrolysis. The data indicates that the mineralization of organic N is greater. According to the total N recovery data, 24-41 % of the pristine CVD N is missing. The N loss is likely due to deamination of amino acid functional groups in protein-like moieties present in pristine CVD. This reaction is expected to yield volatile ammonia, which is lost in the gas phase, and residual carboxylic organic C groups. A smaller fraction of carboxylic groups would decarboxylate to CO_2, which remains as carbonate in the alkaline reaction medium. No gas phase analysis was performed. The available data do not allow assessing the rate of volatile ammonia generation. Nevertheless, it shows that from 65 to 70 % organic C and N are recovered at 150 °C in soluble form. No significantly higher yield of soluble organic C and N was observed at higher temperature.

3.1. Chemical composition of the soluble product as a function of reaction temperature.

Chemical composition was analysed for the SBO R5 fractions, which were separated from the P5 fractions, as described in section 2. According to this description, R5 was expected to contain most of the pristine SBO organic matter, with P5 containing most of the added KOH reagent. Table 3 shows that R5 dry matter, C and N yields increase by 2.5 fold upon increasing the reaction temperature from 60 to 150 °C, while P5 dry matter, C and N yields are constant or change much less. The R5 yield increase is consistent with the raw SBO yield increase (Table 2). Table 4 shows the vis-a-vis comparison of the values for the total dry matter, C and N recovered with R5 and P5, relatively to pristine CVD, with the values measured for the raw SBO. It appears that, upon filtration, the raw SBO matter is entirely recovered and distributed over R5 and P5. Table 5 shows that R5 contain more C and N than raw SBO (Table 1). This results from the filtration through the 5 kDa membrane, which separates P5 containing the excess added KOH. However, C/N ratios for R5 (Table 5) and raw SBO (Table 1) recovered at each temperature are quite close. They are within the 8.47 ± 0.42 range, which Rosso et al. (2015) assumed to indicate no difference in the chemical nature of SBO products from different source. Thus, R5 organic matter largely represents the raw SBO organic matter.

The results of SBO filtration indicate that its major fraction is polymeric. Compared to R5, P5 contains much more inorganic C. Typical data for the 150 °C R5 and P5 fraction indicated that nearly equal amount of dry matter are recovered with each fraction (Table 3). However, P5 dry matter contains 11.4 w/w % inorganic C, corresponding to 95 w/w % $KHCO_3$, whereas R5 dry matter contains 1.1 w/w % inorganic C, corresponding to 9.2 % $KHCO_3$. Moreover, 94 % of the water contained in the pristine SBO solution fed to the membrane was recovered with the P5 fraction. This contained 1.9 % dry matter versus 26 % dry matter in the R5 fraction. Both fraction had nearly the same pH of 9.6 and 9.7 respectively. The data indicates that most P5 content is inorganic, mainly constituted by the excess alkali over the amount bonded to the R5 organic matter. This prospects that, in real operation, P5 could be recycled to the hydrolysis reactor to treat new CVD. In this fashion, the alkali consumption would be reduced to the amount bonded to R5 organic matter. Most process solvent and reagent could be reused without secondary treatment of process effluent. Moreover, further process energy savings would result from the lower amount of water to evaporate for obtaining solid R5.

3.1.1 Molecular weight measurements

For R5, Table 5 reports weight average molecular weight (M_W), polydispersity index (M_W/M_N), and % total mass recovered from the SEC column used for these measurements (see section 2). The 91-96 % mass recovered indicates that the reported M_W and M_W/M_N data are largely representative of the total sample matter. The M_W data reported in Table 5 indicates an apparent increase of molecular weight for 100 and 150 °C R5, compared to 60 °C R5. The molecular weight increase at 100-150 °C may result from condensation and/or cross-linking reactions of the product obtained at lower temperature. Depolymerization of lignin to soluble fragments and their repolymerization are known in lignin chemistry, depending upon experimental conditions (Fang et al., 2008).

3.1.2 C types and functional groups measurements

The C and N values for R5 (Table 5) are very close to those for raw SBO (Table 1). This confirms that R5 largely represents most of SBO organic matter. This data, together with 13C NMR spectroscopy and potentiometric titration data, allowed calculating the distribution of the identified C types and functional groups over the three 60, 100 and 150 °C R5 products.
    Table 6 reports chemical features for R5, IR and CVD. It lists the C moieties identified by 13 C NMR spectroscopy, each quoted as % of total integrated band area. Products and CVD contain the same C types and functional groups, but in different relative ratios. Compared to CVD and IR, R5 contain relatively more Ph and carboxylC, but less alkoxy C. The IR organic matter is more similar to CVD organic matter. The different chemical composition of R5 suggests that IR contain the residual recalcitrant organic matter. This is present in CVD and is characterized by not hydrolysable ether bonds linking aromatic and aliphatic C moieties.
    Table 7 reports a further breakdown of Table 6 data. It results from integrating Table 6 13C NMR data with Table 5 C and N data, and with potentiometric titration data. The three carboxylic acid groups X_1, X_2 and X_3 (see section 2 and supplementary material SM file) have been tentatively assigned to the functional groups fragments reported in the Table 7 footnote. Keeping in mind the limitations set forth by the complex SBO composition, the carboxylic acid assignements should be viewed as virtual. Nevertheless, they are well consistent with 13C NMR data in

Table 6. They offer a plausible explanation of the different surface activity among the R5 products (see section 3.1.3 below). Moreover, the data for 60 °C R5 in Table 7 are quite close to those for R5 obtained in the CVD 60 °C hydrolysis by conventional heating (Montoneri et al., 2016). This fact, suggests that the product obtained in the MW assisted and in the conventional hydrolysis at the same temperature are similar.

3.1.3 Surface tension properties

The ability of a product to lower the surface tension of water is a basilar property, which allows predicting the potential product value as surfactant, and therefore in the many applications where surfactants are used. Fig. 1 shows the plots of the water surface tension (γ) versus the added product concentration (C_{R5}), for 60, 100 and 150 °C R5. The trend of γ decrease upon increasing C_{R5} is typical of surfactants. The plots show that, at equal C_{R5}, the order of increasing surface activity is R5 (150°C) > R5 (100°C) > R5 (60°C). Thus, the products performance as surfactant improves upon increasing the temperature of the reaction producing it.

Table 7 provides further information about the products' performance order. Fig. 2 depicts a virtual molecular fragment, which fits the analytical data obtained for the 150 °C R5 product. The fragment does not represent the real chemical structure of R5 organic matter. Most likely, R5 is a mix of molecules with different molecular weights and distribution of functional groups. The depicted fragment may help understanding the behavior of these molecules in water and their relation with the surface tension properties. Table 7 and Fig. 2 show four types of acid groups, with acid strength increasing in the order, phenol < amino carboxylic acid < aliphatic or hydroxyl carboxylic acid < and aromatic or di-carboxylic acids. The 150 °C R5 has the highest content of total carboxylic groups, 38 % of which contributed by aliphatic and/or hydroxyl carboxylic acid (R'COOH). By comparison, in the 100 and 60 °C R5, R'COOH represent 29 and 25 % of the total carboxylic groups. The order of increasing R5 surface activity seems directly related to the R'COOH content. However, data published on SBO obtained from different biowaste materials (Montoneri et al., 2014) and on oxidized SBO obtained from CVD (Montoneri et al., 2016) shows that, for these complex molecular pools, a correlation of surface activity with a specific functional groups cannot be established. In the specific case of R5, it may be observed that the other acid groups do not seem correlated with the order of surface activity. Evidently, both the relative content and type of acid groups, and the composition of the moietites including the acid groups, are important in determining the product performance as surfactant. The order of increasing R5 surface activity reflects also the order of increasing PhOY, Ph and Af concentration in Table 7. On the other hand, it reflects also the order of decreasing content of OR and OCO groups. The data indicates that, for the R5 molecular pools, the R'COOH, Ph, PhOY, Af, OR and OCO C moieties appear the major chemical factors ruling the products hydrophilic-lipophilic balance, and therefore their surface activity. For the scope of the present work, it is enough learning that the product obtained at 150 °C has equal or better surface activity properties of the products obtained at lower temperature. Assessing a definite surface activity-chemical composition relationship for SBO products requires collecting a large number of data over SBO from different sources, which exhibited different chemical composition.

3.2. Process energy analysis

The following systems were tested in the microware reactor (see Methods) under the same conditions: water (A), water with added KOH (AC), water with added CVD compost (AB), water with added CVD compost and KOH (ABC). The amounts of each component was the same in all tested systems. The applied power was 50 W to heat up the four systems from the initial temperature (Ti) to 60 and 100 °C, and 50 and 100 W to 150 °C instrumental set point temperature (Ts) values. Under these conditions, the end temperatures (Te) were reached within 273 seconds, and no evident over heating occurred with gas pressure increase over the equipment measurable range. At applied power > 100 W, excess unmeasurable gas pressure developed at 150 °C, due to the occurrence of an exhotermal reaction.

Fig. 3 shows the delay of ABC at 100 W applied power to reach 150 °C Te, compared to the other systems. Moreover, ABC exhibits the abrupt increase of the plot slope at 130 °C leading to overheating above Ts. The plot (not shown) at 50 W applied power is qualitatively similar, except for lower slope increase at 130 °C. The slope increase in the plot (not shown) for ABC at 100 °C Te was less evident, but still observable starting at about 90 °C. Fig. 4 shows that, at 150 °C Ts and 100 W applied power, AB and ABC reach higher autogenous pressure than A and AC. The pressure reached by A and AC corresponds roughly to the vapor pressure of water. ABC, followed by AB, reaches the highest pressure. The pressure increases of ABC and AB, compared to A and AC, amount to 3 and 1.5 bar, respectively. The ABC system exhibits an abrupt pressure increase at the same time of the increase of the slope of the temperature versus time plot in Fig. 3. For the experiments at 60 and 100 °C Ts, no or negligible pressure over atmospheric pressure was recorded. The pressure data at 150 °C Ts suggests that the compost hydrolysis and organic matter decomposition reactions occur both in the presence and in absence of KOH. Data (not shown), obtained for the reaction performed in absence of KOH, demonstrated that the SBO yields were 5-6 %, relatively to CVD, showing no definite trend upon increasing temperature. On the contrary, Table 2 (section 3.1) shows that, in the presence of KOH, the reactions are more relevant.

Both the pressure and abrupt temperature increases of ABC at 150 °C Ts are consistent with the occurrence of an exothermal reaction. Heat release can happen from both decomposition and recombination reactions. The total C and N recovery values with the reaction products in Table 2 indicate higher loss of organic N than organic C. This suggests (see section 3.1) the occurrence of a decomposition reaction, with release of gaseous ammonia. Based on the reaction N loss reported in Table 2 for Ts 150 °C, 1.14 ammonia mmoli would be released in the gas phase. Considering 10 ml free volume in the reaction vessel (see section 2), the pressure developed at Te corresponds to the higher pressure reached by ABC compared to the A system. On the other hand, the molecular weight data in Table 5 suggest the occurrence of a repolymerization reaction, which occurs at 100-150 °C between the products obtained at lower temperature. This reaction may also cause or contribute to the observed heat release in Fig. 4. More details on the process energy analysis are reported in the SM file.

3.3. Constraint of lignin hydrolysis

A major problem in biomass valorization as source of value added compounds is the presence of recalcitrant lignin or lignin-like material. The data collected in the present work shows that a maximum 70 % organic C of the pristine compost is converted at 150 °C to the valuable SBO. Similar constraint is reported for the hydrolysis of biomass from other different sources, e.g. wheat (Janker-Obermeier et al., 2012) and triticale (Monteil-Rivera et al., 2012) straw, walnut shell (Liu et al., 2006), sawdust and rice husk (Karagoz et al., 2005), rice bran (Pourali et al., 2010), and several other biomass residues (Zhang et al., 2008). Most of them were treated hydrothermally at 200-400 °C, i.e. under even more drastic

conditions than in the present work. Complete conversion of pristine lignin matter to value added products was never achieved. Depending on the sourcing material, different small molecule phenolic compounds were obtained. Residual insoluble solid matter ranged from 10 to 60 %. No biopolymers as SBO have been reported. Yet, even from agriculture residues, 60 °C hydrolysis has been shown to yield SBO-like products (Franzoso et al., 2015). The data from the above authors and the results of the present work suggest that at low temperature (60-200 °C) the lignin materials is hydrolyzed to soluble polymeric fragments, which keep the memory of the pristine lignin. At higher temperature (200-400 °C), the polymeric soluble fragments are further broken down into small molecules.

   The fact that in all cases, hydrolysis of biomass containing lignin-like matter yields an insoluble residue may arise for two reasons. One is that high temperatures promote the depolymerisation of lignin to soluble and/or liquid fragments, while long reaction times facilitate the reaction between these fragments and high molecular weight insoluble polymers (Fang et al., 2008). The other is that the insoluble organic matter contains chemical bonds, which cannot be hydrolyzed further to obtain soluble compounds. The insoluble matter may be produced during hydrolysis or may constitute a fraction of the pristine lignin material. Under these circumstances, further conversion of the insoluble solid residue requires application of thermochemical reactions, such as pyrolysis or gasification, in order to increase its conversion to value added aromatic platform molecules.

4. Conclusion

   For the investigated compost hydrolysis at 60-150 °C, the main reaction products are water soluble biopolymers (SBO) with useful surfactant behavior. Product yield increases upon increasing reaction temperature. It reaches 70 % at 150 °C. The SBO yield is limited by the presence of non-hydrolysable lignin-like matter in the pristine compost. The collected molecular weight, chemical composition and surface activity data shows that the SBO chemical chemical composition is moderately affected upon increasing temperature from 60 to 150 °C. Rather interesting and attracting is the fact that the SBO obtained in the highest yield at the highest temperature seem to exhibit the best properties as surfactants. The reaction energy analysis has evidenced the occurrence of an exhotermal reaction, likely due to organic matter decomposition. The connected pressure increase rate has been shown to depend on temperature and on the applied power. At 100 W and 150 °C, it has been possible to measure 60 % pressure increase over the water vapour pressure. The collected data prospects the feasibility to scale up to commercial production level a sustainable process, allowing solvent and reagents recovery and recycling without secondary treatment of liquid effluents. Under industrial production conditions, the potential risk of the exothermal runaway reaction has to be considered. This may be managed safely by controlling temperature and applied power. The process is likely applicable to biomass from different sources. Relatively to current knowledge on the hydrolysis at 200-400 °C of biomass from different vegetable sources, the results reported in this work prospect that hydrolyzing biomass at lower temperature allows maintaining the memory of the polymeric chemical structure of the native lignin proximate, while converting it to soluble form and producing valuable polymeric speciality chemicals and spending less energy.

Acknowledgement

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Table 1

Analytical data[a] as w/w % in dry matter for products (SBO and IR) obtained by CVD hydrolysis at different temperature (T, °C).

T,°C	Ash		Organic C		N		Organic C/N		Inorganic C	
	SBO	IR	SBO	IR	SBO	IR	SBO	IR	SBO	IR
60	65.8±3.85a	73.8±1.73a	18.3±1.21a	10.9±1,68a	2.1±0.16a	0.8±0.16a	8.7±0.28a	13.3±1.11a	3.4±0.34a	0.5±0.05a
100	60.1±1.31ab	73.6±2.41a	22.2±0.77b	12.1±1,84a	2.9±0.12bc	0.7±0.16a	7.8±0.05b	16.8±1.71b	2.5±0.31b	0.5±0.06a
150	54.8±1.72b	78.8±2.60a	25.3±0.31c	10.3±2.96a	2.8±0.04c	0.3±0.06b	8.9±0.24a	31.6±3.28c	2.1±0.25b	0.7±0.07b

[a]Average of triplicates±standard deviation; within each column, values followed by different letters are significantly different at $P < 0.05$ level.

Table 2
Material balance[a] for CVD hydrolysis at different temperature (T, °C) as w/w % recovery with SBO and IR products, relative to starting CVD compost[b] and added KOH.

T,°C	Dry matter			Inorg C			Org C			N		
	SBO	IR	TOTAL	SBO	IR	TOTAL	SBO	IR	TOTAL	SBO	IR	TOTAL
60	33.0±0.72a	66.5±0.45a	99.6±1.13a	6.0±0.13a	1.6±0.01a	7.6±0.77a	34.0±1.56a	40.9±6.04a	74.9±6.01a	32.8±1.79a	26.1±4.70a	58.9±6.49a
100	41.3±0.69b	57.7±0.79a	99.0±1.35a	5.5±0.09b	1.5±0.02a	7.0±0.70a	51.7±1.13b	39.3±5.48ab	91.0±5.33b	55.7±1.58b	19.9±4.19a	75.6±5.77bc
150	47.9±0.32c	43.6±7.59b	91.4±7.29a	5.3±0.04b	1.7±0.29a	7.0±0.53a	68.3±1.20c	24.4±2.16b	92.7±2.73b	64.4±0.61c	6.5±0.12b	70.9±0.43ac

[a]Average of triplicates±standard deviation; within each column, values followed by different letters are significantly different at $P < 0.05$ level. Values followed by two letters are not significantly different from values having in common one of the two letters. [b] Pristine CVD contained 56.1 ash, 22.3 organic C, 1.17 inorganic C, and 2.7 N w/w % relative to dry matter.

Table 3

Recovery (w/w %) of dry matter, organic C and N yields (relative to the starting CVD dry matter, and organic C and N), and of ash (relative to the starting ash in the CVD dry matter and added KOH) with the retentate (R5) and permeate (P5) fractions isolated by filtration through 5 kDa polysulphone membrane of SBO obtained at different temperature (T).

T, °C	R5			P5		
	dry matter	C	N	dry matter	C	N
60	9.1	19.5	20.1	26.6	14.6	7.5
90	16.3	36.1	38.3	25.4	12.3	8.2
150	22.8	50.5	48.3	27.0	17.9	12.7

Table 4

Total dry matter, C and N recovered with SBO at 60, 100 and 150 °C reaction temperature (T), compared to the total dry matter, C and N values recovered with the corresponding R5 and P5 fraction. Values are expressed as w/w % of starting CVD dry matter, organic C and N, respectively.

T, °C	R5 + P5			SBO		
	dry matter	C	N	dry matter	C	N
60	35.7	34.1	27.6	33.0	34.0	32.8
90	41.7	48.4	40.5	41.3	51.7	55.7
150	49.8	68.4	61.0	47.9	68.3	64.4

Table 5

Analytical data for Table 3 R5 fractions obtained from crude SBO recovered from the CVD hydrolysis at 60, 90 and 150 °C temperature (T): organic C and N in % weight of dry matter, weight (M_W) and number (M_N) average molecular weights in kDa, and polydispersity index (M_W/M_N).

T,°C	C, w/w %	N, w/w %	C/N	M_W, kDa	M_W/M_N	Recovered Mass, w/w %[a]
60	37.3	4.6	8.1	93.3	1.28	95.8
100	38.8	4.8	8.1	158	1.50	95.4
150	38.6	4.3	9.0	133	1.34	91.0

[a]Mass recovered from SEC column relative to the starting sample amount (see Methods)

Table 6

C types and functional groups[a] for CVD and products[b] obtained from CVD hydrolysis at 60, 90 and 150 °C: i.e. Table 3 R5 fractions and corresponding insoluble products (IR).

δ, ppm	Data from ^{13}C NMR spectroscopy: signal chemical shift (δ, ppm), assignment to C type and integrated relative band area %[a]							
	0-53	53-63	63-95	95-110	110-140	140-160	160-185	185-215
C type[a]/ Product[b]	Af	NR+OMe	OR	OCO	Ph	PhOX	COY	C=O
R5-60	36.2	8.10	15.9	4.67	12.6	5.15	15.2	2.08
R5-100	42.1	7.68	8.88	3.00	13.8	5.02	16.8	2.60
R5-150	43.7	8.55	8.46	2.71	15.7	5.87	13.1	1.82
IR-60	35.1	8.05	27.3	4.89	9.24	4.16	8.08	3.12
IR-100	35.3	8.02	27.3	4.24	8.17	4.64	7.76	4.52
IR-150	26.7	9.18	33.0	6.65	9.18	5.53	4.80	5.03
CVD	37.2	9.75	28.1	4.35	8.11	5.20	6.67	0.62

[a]Data for aliphatic (Af), aromatic (Ph), phenol and/or phenoxy (PhOX, X = H, alkyl and/or aryl), methoxy (OMe), carboxyl (COY), amine (NR), alkoxy (RO), anomeric (OCO), and keto (C=O) carbon; R = alkyl, X = H, alkyl and/or aryl, Y = OH and/or amide N, Ar = Ph + PhOX. [b]Product identified according to the temperature of the reaction from which the pristine SBO was obtained.

Table 7

Further breakdown of C types[a] and functional groups[a,b] in meq/g for Table 3 soluble R5 fractions, calculated from ^{13}C NMR spectra, microanalytical C and N, and potentiometric titration (see Methods).

C type[a]/ Product[b]	Af	OMe	NR	X_1	OR	OCO	Ph	PhOH	PhOY	X_2	X_3	CON	C=O
R5-60	11.2	0.70	0.80	1.02	4.94	1.45	3.92	0.49	1.11	0.81	1.44	1.46	0.64
R5-100	13.6	1.19	0.00	1.29	2.87	0.97	4.47	0.46	1.16	0.94	0.98	2.23	0.84
R5-150	14.0	0.17	1.48	1.09	2.72	0.87	5.05	0.57	1.31	1.41	1.22	0.50	0.58

[a]Data for aliphatic (Af), methoxy (OMe), amine (NR), amino carboxylic acid (X_1 = N-C-COOH), alkoxy (RO), anomeric (OCO), aromatic (Ph), phenol (PhOH), phenoxy (PhOY), aliphatic and/or hydroxyl carboxylic acid (X_2 = R'COOH), aromatic and/or dicarboxylic acid (X_3 = R''COOH), amide (CON) and keto (C=O) carbon; R = alkyl, Y = alkyl or aryl, R' = alkyl and/or α-hydroxyl alkyl, R'' = aromatic, and/or aromatic and/or aliphatic C substituted with second COOH functions; [b]Product identified according to the temperature of the reaction from which the pristine SBO was obtained.
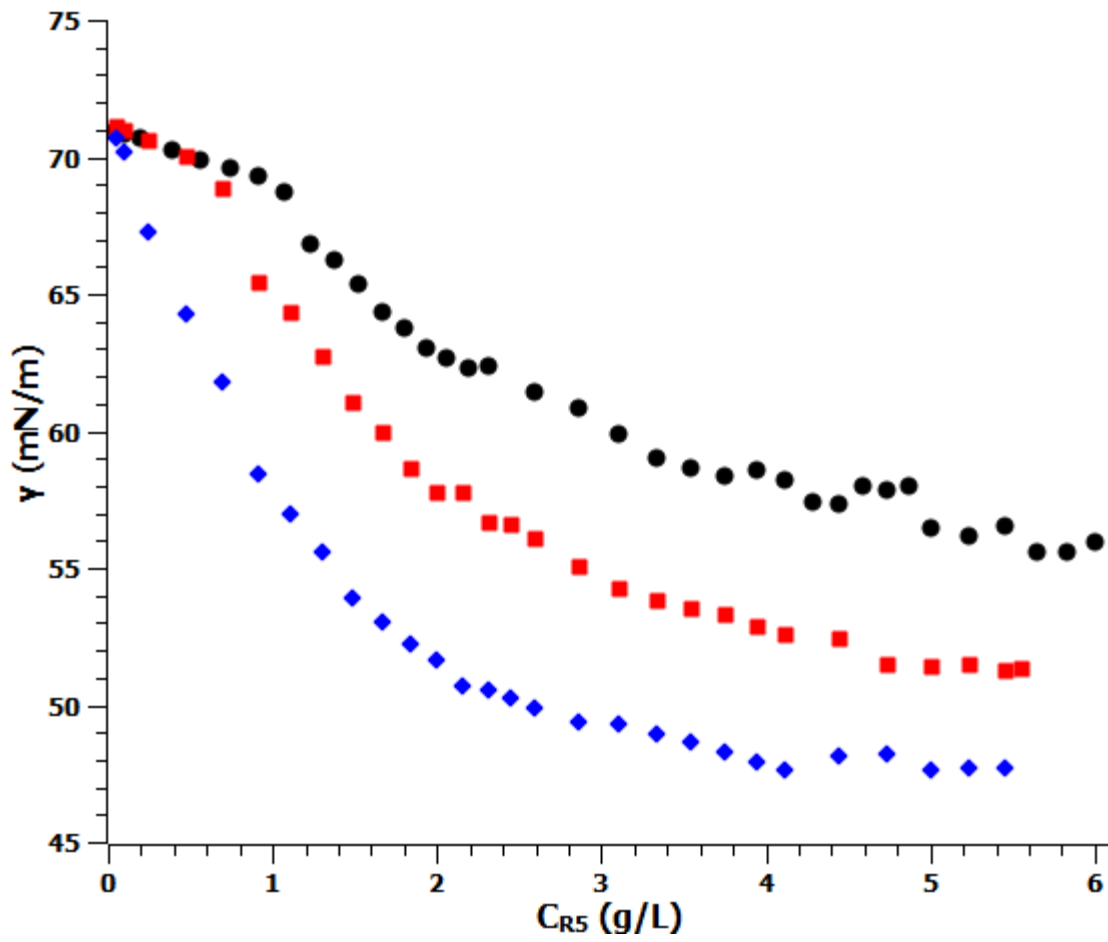
Fig. 1. Water surface tension (γ) versus added concentration (C_{R5}) of R5 obtained at 60 (●), 100 (■) and 150°C (◆).
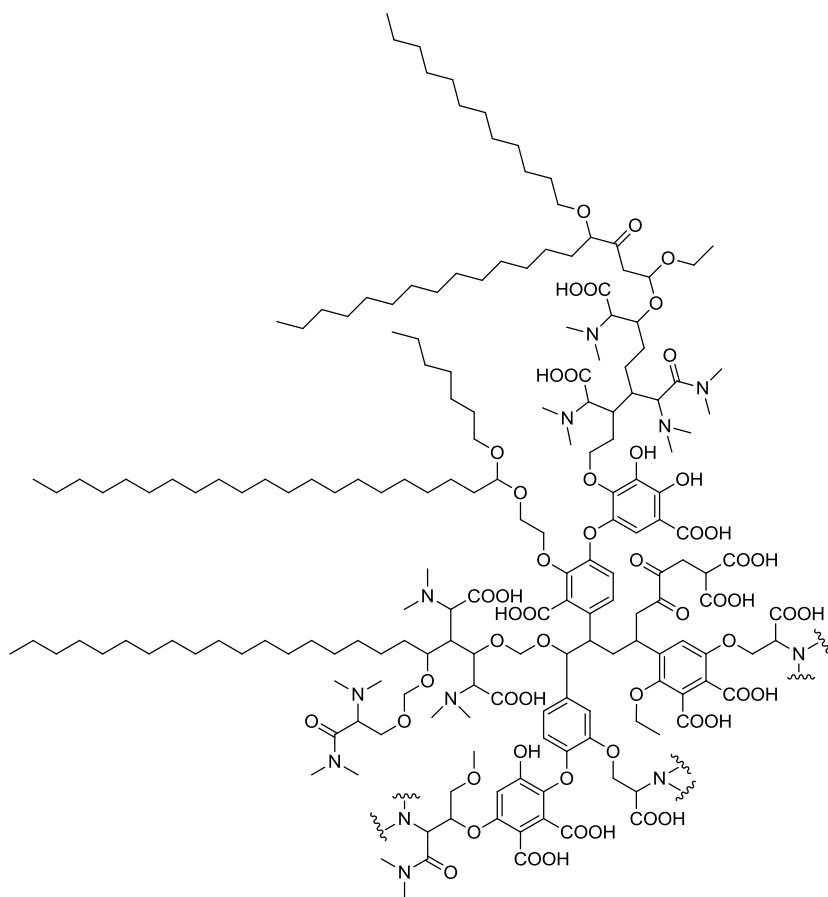
Fig. 2. Virtual molecular fragment fitting the analytical data for 150 °C R5 in Table 7.
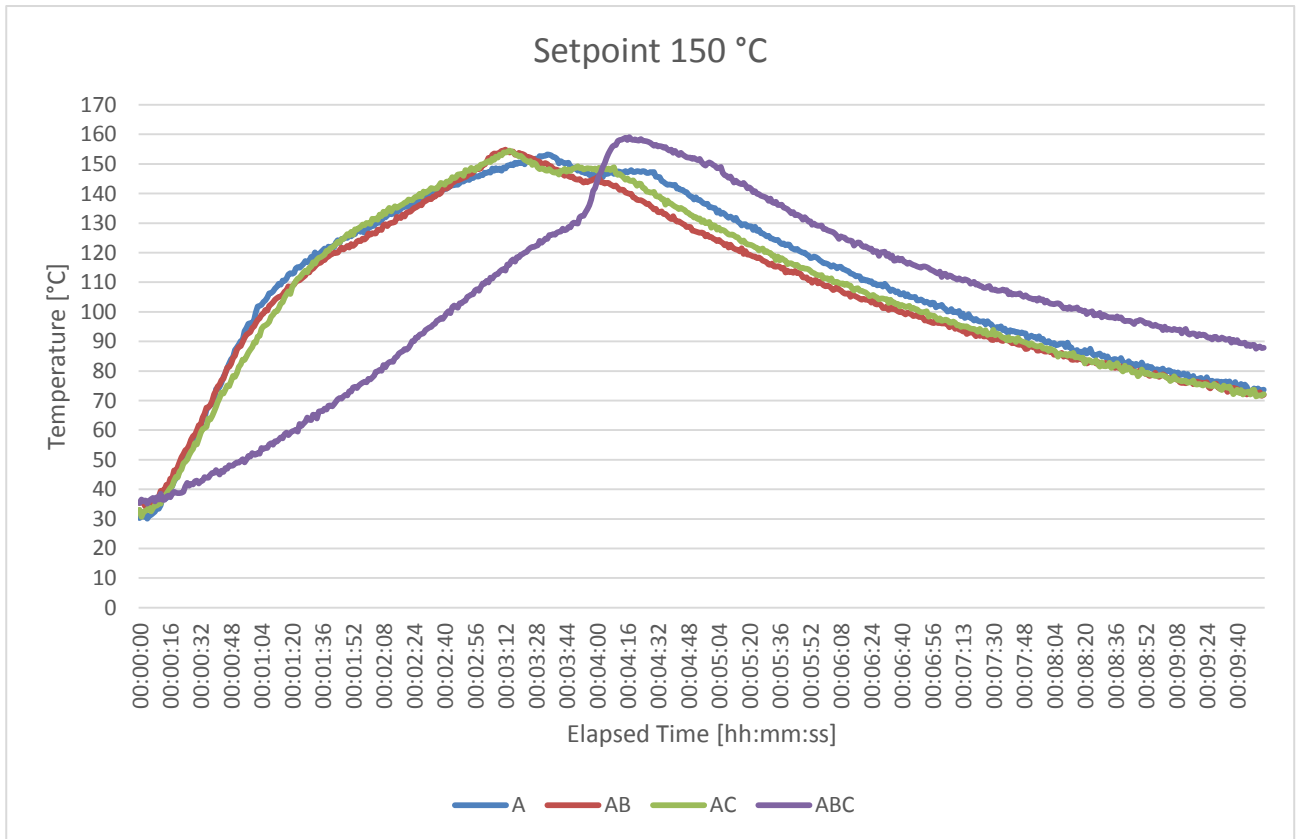
Fig. 3. Temperature versus time plot for the four investigated systems at Ts 150 °C and 100 W applied power (legends in text).

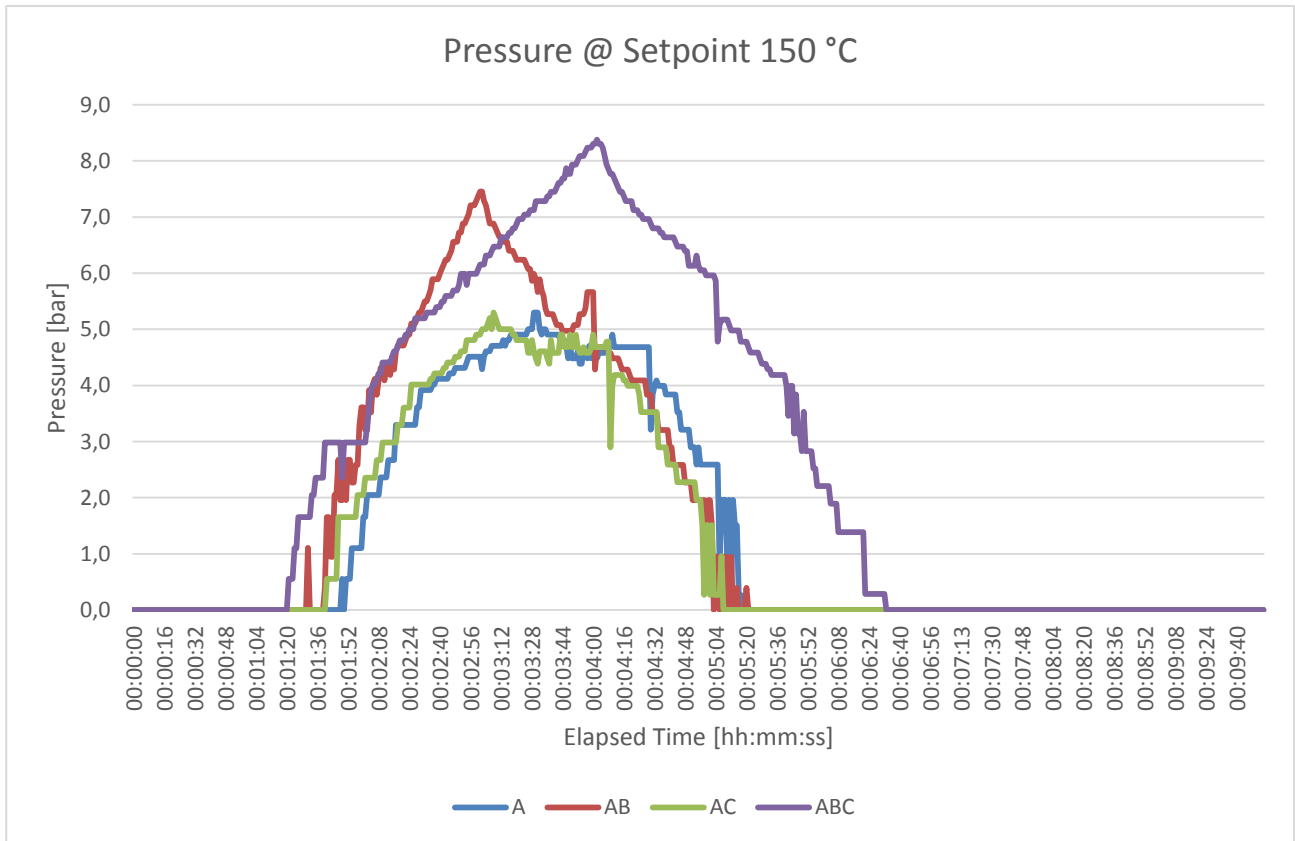**Fig. 4**. Pressure versus heating time for the four investigated system at 150 °C Ts and 100 W applied power.