CHEMICAL ENGINEERING TRANSACTIONS

VOL. 65, 2018

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Eliseo Ranzi, Mario Costa

ISBN 978-88-95608- 62-4; **ISSN** 2283-9216

Pressurized Steam Torrefaction of Wet Agro-industrial Residues

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This paper aims at demonstrating the viability of pressurized steam torrefaction (PST) as an effective pre-treatment of wet agro-industrial residues for a flexible generation of biochar, along with secondary liquid products as “green” feedstocks of interest in chemical and process industries.

A comprehensive experimental investigation program is presently going on at a laboratory scale by testing two wet agro-industrial residues typical of Italian agro-food sector, i.e., tomato peels and olive husks, produced in the Campania region (Italy). As a complement to the batch pressurized treatment in presence of water, the addition of a simple and cheap catalytic material has been taken into consideration during the torrefaction stage, and before the subsequent stage of solvent extraction of chemicals from the non-volatile torrefied products. This article reports the work-in-progress results, which are in the direction of boosting and upgrading the produced liquid fraction.

1. Introduction

The torrefaction is a thermal pre-treatment of biomass and other carbonaceous materials aimed at their conversion into a commodity solid fuel with more uniform and standard properties. During torrefaction, the feedstock biomass is heated in an inert environment up to moderate temperature, ranging between 200 °C and 300 °C (Kuzmina et al., 2016). Even though short reactor residence times are more desirable for industrial application, slow particle heating (typically less than 50 ° C/min) and rather long residence times (typically ranging between 30 and 120 min) have been originally suggested for torrefaction in order to ensure a high yield of the solid product (Brachi et al., 2016).

It is well known that drying is strictly required for chemical and biological stabilization of wet residual biomass materials that originate from agro-industrial activities, like grape waste, distillation sludge, olive husks, tomato residues, etc. Water removal to a large extent is a pre-requisite to any thermochemical conversion process (Miccio et al., 2016), including torrefaction (Barletta et al., 2017). Conventional drying is carried out with hot air and represents a high-cost pre-treatment. Alternatively, drying with steam at atmospheric (superheated steam drying, SHD) and above atmospheric pressure (pressure steam drying, PSD) have been largely applied in different cases at both pilot and industrial scales, due to improved heat transfer properties with respect to air. Using superheated steam as drying medium allows improving the process performance of both treatment time and energy consumption. A major advantage of pressure drying is the ability to allow a fast feedstock treatment without over-drying its surface (Wimmerstedt, 1995).

In the above contest, the idea of avoiding drying, but taking advantage of pressure operation in the pre-treatment of wet residual biomass materials appears as a new appealing route. To this end, pressurized steam torrefaction – a novel pre-treatment – deserves consideration: its concept is based on heating the feedstock under pressure and using the inherent water, or steam generated by it, as a reactant. It could ensure possible operational advantages with respect to the atmospheric process, in terms of faster treatment, energy consumption, and quality of solid/liquid products (Xiao et al., 2015; Agar et al., 2016). Moreover, unlike conventional torrefaction techniques, where flue gases are used for direct heating, steam torrefaction does not contaminate the torrefied solid and the volatile matters, disclosing a way to recovering valuable chemicals. Brachi et al. (2017) recently demonstrated that pressurized torrefaction can yield a larger fraction of liquids from the biomass feedstock, in particular if associated with a further stage of chemical extraction by a solvent (i.e., acetone). However, the need to produce steam would impact the design and energy demand of the reactor, so moderate temperature (i.e. < 250 °C) is recommended (Brachi et al., 2017).

The introduction of a catalyst (e.g., for hydrocarbons and by-products conversion) could represent a suitable strategy to increase the quality of the products also during the torrefaction process. Among the catalysts proposed for the upgrade of pyrolysis products, CaO represents a simple, cheap and effective option due to its low working temperature in comparison to those required by ZMS-5 based systems (Kabir and Hameed, 2017). Recently, the use of Al_2O_3 has been also proposed, with promising results, for upgrading the pyrolysis products of Karanja seeds to bio-fuels (Prasad and Shadangi, 2014).

The results of a first experimental campaign on pressurized torrefaction in presence of catalyst are reported and discussed in the following.

2. Experimental description

2.1 Materials

Two agro-industrial residual biomass produced in Campania region (Italy) were considered: 1. tomato peels (TP) from conventional tomato processing and 2. virgin olive husk (OH) from a three-phase olive mill. Both materials are seasonal. They have an initial moisture content higher than 50% by weight, corresponding to a water/dry-biomass ratio much larger than 1. For a better handling in the experimental campaign, the tested biomasses were air-dried in a ventilated oven for a couple of days down to residual moisture fraction of about 6% wt. Before and after air-drying, the moisture content of samples was checked by means of a Kern DBS Halogen Moisture analyzer, which heats the sample up to 120 °C. Air-dried biomass samples were then subjected to grinding in a batch knife mill (Grindomix GM 300 by Retsch) for about 20 s at a speed of 3200 rpm (TP) or alternatively in a cutting mill (Fritsch Pulverisette 15-OH). The milled samples were finally sieved, the 1.0-2.0 mm size fraction being selected for the torrefaction tests with both materials. The main physical-chemical properties are reported in Table 1. Both biomass materials exhibit a rather high heating value on a dry basis. It is worth noting the very low tap density of the tomato peels (< 0.1 g/mL) that hinders an easy utilization of the material in real processes.

Table 1: Properties of the biomass feedstocks (on a dry basis)

	Particle size mm	Tap density g/mL	C %	H %	N %	O %	Char %	Vol. %	Ash %	LHV MJ/kg
Olive Husks	1.0-2.0	0.35	54.4	6.8	0.8	35.3	18.9	78.4	2.7	22.5
Tomato peels	1.0-2.0	0.09	58.4	7.7	1.5	30.1	13.4	84.3	2.3	23.8

2.2 Experimental setup

Torrefaction tests were carried out in a lab-scale, batch pressurized tubular reactor made in AISI 316 stainless steel (21 mm inner diameter, 200 mm height, 48 mL internal volume), as showed in Figure 1. A pressure indicator and a K-type thermocouple are connected to the reactor, allowing to measure the temperature (T) and the pressure (P) inside the reactor. During each test, a dry sample of prefixed weight (1.0 or 2.0 g) is placed in a glass test tube and distilled water is added to the solid in order to achieve a prefixed value of the water-to-dry-biomass mass ratio. In some tests a catalyst powder in the amount of 1 g (< 100 μm size) is added on the top of the biomass layer. A wad of ceramic fiber wool is used to close the test tube before putting it into the stainless steel reactor tube, which is finally sealed. To ensure an inert atmosphere, the chamber is purged by blowing argon more times throughout a needle valve. Afterwards, the stainless steel reactor is inserted into an electric tubular furnace (CARBOLITE 1200, Fig. 1, left). Upon heat-up, the oven temperature is set at a fixed value in the range of interest for torrefaction, while the temperature and pressure inside the reactor vessel are continuously monitored.

The reactor is kept closed during the whole test time allowing an increase in pressure, as consequence of water evaporation and the release of volatile matter from the biomass, in parallel with gas expansion. After the prefixed residence time (1 h) has passed at a stable value (±5 °C) of the prefixed temperature, the steel reactor is quickly extracted from the tubular furnace and cooled in cold water. Then, the residual gas is expanded into a graduated syringe by opening the needle valve; this allows determining the volume $V_{G,st}$ at standard conditions (20 °C) of the generated gas phase. Finally, the reactor is opened and the glass tube removed for subsequent steps.

The whole sample of the torrefied biomass recovered from the glass tube is treated with acetone for the extraction of the condensed soluble compounds (1 day), with subsequent filtration on a paper filter (Whatman 43). Thus, two samples are obtained: a residual solid fraction and a liquid solution of acetone containing the extracted species. The former is subjected to proximate analysis, whilst the latter is qualitatively characterized by means of an Agilent GC 7890A gas-chromatograph equipped with a MSD 5975A flame ionization detector.

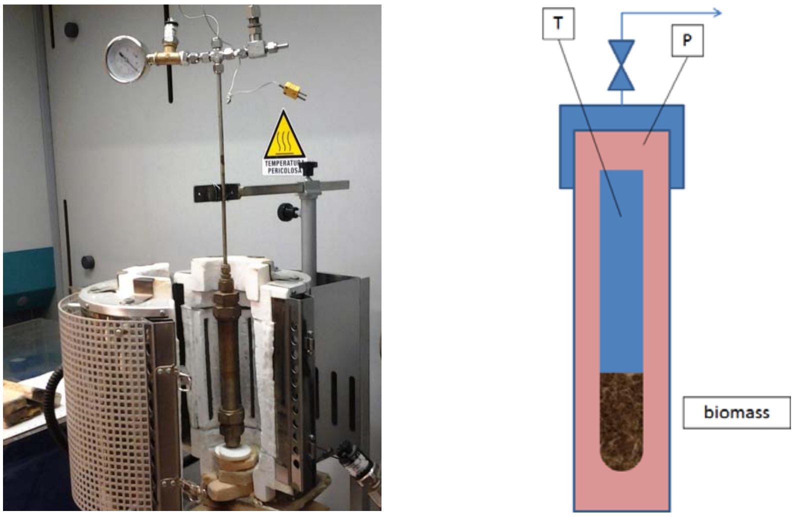

Figure 1: Photograph (left) and schematics (right) of the experimental setup for pressurized torrefaction tests.

3. Experimental results

The operating conditions and main results of the pressurized steam torrefaction tests with both biomasses (OH and TP) are reported in Table 2. The tests listed in Table 2 are divided on the basis of biomass type (OH vs. TP) and absence/presence of a catalyst in the reactor. In the 5th column the pressure recorded at the end of each test lasting 1 hour at constant temperature (column 4) is also reported.

The yields in solid (Y_S), liquid (Y_L) and gas (Y_G) phases are computed according to equations 1-3 on the basis of the samples obtained upon extraction in acetone, filtration and drying of the residual solids.

$$Y_S = M_{S,dry}/M_{0,dry} \tag{1}$$

$$Y_G = \frac{V_{G,st}\ W_G}{24.4\ M_{0,dry}} \tag{2}$$

$$Y_L = 1 - Y_S - Y_G \tag{3}$$

where $M_{S,dry}$ and $M_{0,dry}$ are the solid residue upon filtration and the initial mass of biomass on dry basis, respectively. The average molecular weight of the gas is assumed equal W_G = 38.0 g/mol (Brachi et al., 2017). Some errors affect the calculation of the above yields. As consequence of the presence of high moisture and volatile acetone in both liquid and solid fractions, an error in the experimental procedure may occur due to the uncontrolled evaporation of such compounds from the test samples, which affects the estimation of solid and liquid fractions. Thus an uncertainty of ± 10% with respect to measured value should be assumed for both Y_S and Y_L. The determination of Y_G is affected by the error in the estimation of the molecular weight of the gas fraction, to be assumed less than ±5% (relative). The latter can be also affected by the adsorption of some gaseous species during catalytic tests.

It is worth noting that current tests were carried out at intermediate temperature with respect to OH06 and OH08 (Brachi et al., 2017). The comparison shows that the yields are comparable to that of OH08, this test being conducted at temperature higher than usual for torrefaction, inducing intense pyrolysis. The yields of solid, liquid and gas fraction obtained during the above tests have been compared with those obtained in absence of catalyst in Figure 2 for both feedstocks.

Table 2: operating conditions and main results of the torrefaction tests

	catalyst	H_2O/ biomass	temperature °C	pressure barg	Y_S	Y_L	Y_G	Ψ
1	2	3	4	5	6	7	8	9
OH103	-	1.0	348	28.0	0.35	0.53	0.12	0.79
OH102	Al_2O_3	1.0	340	18.5	0.40	0.53	0.07	0.46
OH106	Al_2O_3	1.0	338	15.0	0.40	0.51	0.09	0.30
OH107	CaO	1.0	330	18.0	0.34	0.65	0.01	0.49
TP102	-	1.0	329	23.5	0.72	0.19	0.09	0.21
TP101	Al_2O_3	1.0	349	21.5	0.66	0.25	0.09	0.17
TP103	CaO	1.0	344	18.0	0.62	0.37	0.01	-
OH06[1]	-	1.0	248	0.0	0.71	0.24	0.05	
OH08[1*]	-	1.2	403	27.5	0.38	0.50	0.12	

[1] from Brachi et al. (2017) * under pyrolysis conditions

The addition of alumina did not significantly affect the product distribution among solid, liquid and gas phases, with respect to non-catalytic tests. The larger change can be noted for TP, where alumina led to an increase of Y_L from to 0.12 (TP102) to 0.25 (TP101), which is likely due to the cracking activity of the catalyst. A more pronounced effect can be observed in the presence of CaO. The liquid yield is further enhanced for both tested biomasses in agreement with that found by Veses et al. (2014). They reported, for large CaO-to-biomass ratio (3:1, 1:1 and 1:2), the promotion of secondary reactions leading to tar formation (i.e., liquid phase) during the pyrolysis process, even if at higher temperature (450°C).

When calcium oxide is used as *in-situ* catalyst, the gas yield is very low. This effect could be due to the absorption of CO_2 produced by the chemical reactions during torrefaction on the calcium oxide itself, according to the classical reaction $CaO(s) + CO_2\,(g) \leftrightarrow CaCO_3\,(s)$. Furthermore, H_2 production may occur from the water-gas shift reaction ($CO\,(g) + H_2O\,(g) \leftrightarrow CO_2\,(g)+H_2\,(g)$) in competition with the methane reforming reaction ($CH_4(g) + H_2O(g) \leftrightarrow 3H_2(g)+CO\,(g)$), with a consequent global effect of lowering the total amount of released gas.

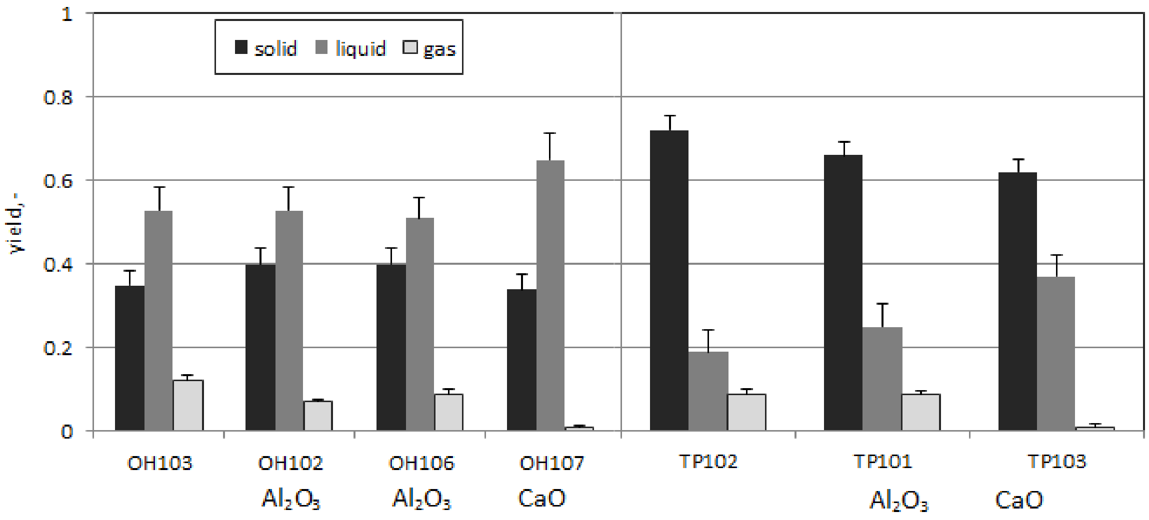

Figure 2: solid, liquid and gas yields obtained during torrefaction tests for OH and TP in catalytic and non-catalytic conditions.

In the case of tomato peels the solid yields are always higher than those obtained for OH under the same experimental conditions, both in absence or presence of catalyst and independently from the catalyst used. This is probably due to the intrinsic nature of OH and TP, in particular the different content in extractives with respect to cellulose, hemi-cellulose and lignin (Brachi et al., 2015; Brachi et al., 2016) . The presence of the catalyst affects Y_L mainly through a reduced generation of the gas fraction.

The index Ψ, which is defined as the ratio of the fixed carbon (C_f) to the volatile matter (VM) normalized with respect to the ash content (X_{ash}), as determined from the proximate analysis of the torrefied dry solid, is reported in Table 2, too.

$$\Psi = \frac{C_f}{VM}(1 - X_{ash})^{-1} \tag{4}$$

Ψ always increases with respect to the characteristic value of both olive husks and tomato peels (i.e., 0.26 and 0.16), confirming that the pressurized, steam-assisted treatment works in the same direction of atmospheric torrefaction. Uncertainties may be attributed in the residual presence of the catalyst in the samples that retained liquid compounds, leading to lower Ψ. The fixed carbon content is much higher in the case of olive husks thanks to its more compact particle structure.

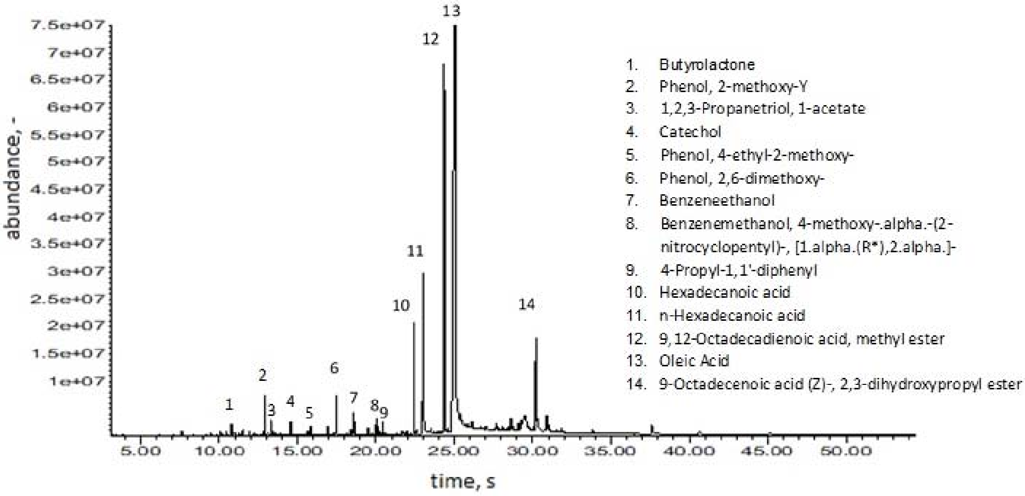

Figure 3: an example of chromatogram from GC-MS analyses carried out on the liquid fraction of the test OH102

The possible effect of the catalyst addition on the composition of the liquid fraction has been investigated by gas-chromatographic analysis, in the case of the OH tests only. Figure 3 shows as an example the chromatogram obtained by GC-MS analyses carried out for the test OH102. As proved by the presence of numerous peaks, a very complex mixture with more than 90 identified species was obtained, the most abundant being indicated in the legend. In order to characterize the extracted species in a semi-quantitative way, the percent area was calculated for each chromatographic peak. Thus, the retention time has been partitioned in suitable intervals, and each liquid component has been attributed to one of the following classes: ketons, aromatics, phenols and fatty acids (mainly palmitic and oleic).

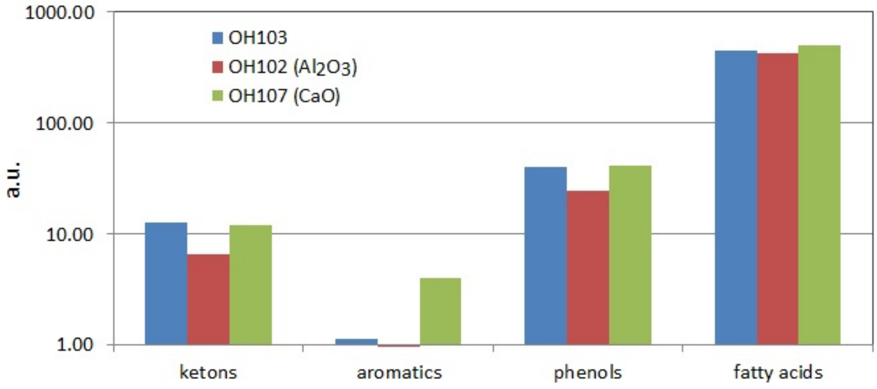

Figure 4: major species detected by gas-chromatographic analyses on the liquid fractions from different torrefaction tests (a.u.: arbitrary unit) for olive husk torrefaction.

The results are reported in Figure 4 in arbitrary units, logarithmic scale on y-axis being used because of the large variation in the order of magnitude. These data demonstrate that the most abundant class is the fatty acids, as expected from the nature of the OH feedstock that is still rich in oil. It can be noted that CaO promotes secondary reactions leading to the formation of heavy organic compounds as oxygenated polyaromatics with a consequent increase in the relative amount of heavy polycyclics observed in the liquid phase (see the “aromatics” bars in Figure 4).

4. Conclusions

The investigated method for a two-stage upgrade of agro-industrial residues, consisting in a first stage of fixed bed, steam-assisted, pressurized torrefaction and a second stage of acetone washing of the non-volatile products, was extended to cope with addition of a catalyst (e.g., alumina and lime) in the first stage.

Confirming previous results under similar conditions of pressure, temperature and residence time, the generation of a liquid phase containing potentially valuable chemicals remains a distinctive feature of the proposed method, but the liquid yield depends on the type of feedstock, peaking up to more than 60% of the initial dry biomass weight in the case of olive husks.

The addition of a catalytic layer above the biomass in the reactor charge seems to have no effect in the case of olive husks, but improves the yield to liquids for tomato peels.

Further research is presently going on to better cover the operating conditions of pressure, temperature and residence time, and to confirm the trends in the reported results. To reduce the experimental uncertainties, online analysis of the generated gas fraction and use of a less volatile solvent will be considered. These future developments will also be addressed to the analysis of scale-up at small factory size (e.g. olive mill), preferably with a semi-continuous process scheme.

Acknowledgments

This research was carried out with the financial support of the MiSE-CNR agreement “Micro co/tri generazione di Bioenergia Efficiente e Stabile (Mi-Best)”

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