# Agro-industrial wastes as a substrate for phenolic compounds extraction followed by pyrolysis

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**Introduction**

In the context of biorefinery, agro-industrial waste can be converted into beneficial products and energy, avoiding final disposal as much as possible. Italy, Spain, and Portugal are the main tomato producers with a share of total European Union (EU-28) production in 2017 of 33, 29 and 9%, respectively. However, the tomato industry generates a large amount of residues during cultivation, packaging, storage, and sale, which includes unripe tomatoes (TWG), rotten ripe tomatoes (TWR) and tomato plant branches (TWB). Also, the wine industry is one of the most relevant socio-economic activities in Europe. Indeed, Italy, France, Spain Greece, and Portugal are responsible for almost 50% of worldwide production. Nevertheless, the winemaking process generates solid wastes composed of grape stalks, skins, and seeds, also named grape pomace (WSW), which requires proper management.

This work aims to evaluate the potential for valorization of tomato and grape pomace residues (TWR, TWG, TWB, WSW) through solid-liquid extraction (SLE) and pyrolysis. This is an innovative study since it assesses the impact of the extraction of phenolic compounds on the thermal conversion of agro-industrial wastes.

**Material and methods**

Rotten ripe tomato (TWR), unripe tomato (TWG) and branches from the plant (TWB)were collected on a local farm. Furthermore, a sample of grape pomace (WSW) was obtained from a winery industry in a central region of Portugal. All samples were dried at 40 ºC, mechanically ground and stored in a dry environment until further use. Total solids (TS) and volatile solids (VS) were determined according to APHA (1998) Standard Methods. Elemental analysis of residues was conducted using Elemental Analyzer NA 2500 equipment. Solid-liquid extraction (SLE) was carried out with 12.5 g of dried sample in 250 mL of ethanol (100%), under stirring conditions for 4 h at 50ºC. After extraction, the liquid phase was separated from the solid, which was dried at 40ºC. The extracted materials are hereinafter referred to as TWRe, TWGe, TWBe, and WSWe. Total phenolic compounds (TPh) were determined by the colorimetric Folin and Ciocalteu method. Pyrolysis assays were performed in thermobalance (TGA/SDTA 851e LF, Mettler-Toledo, Zürich, Switzerland) coupled with a mass spectrometer (MS) (QMS 200 Balzers Thermostar, Asslar, Germany). Pyrolysis was accomplished in an inert atmosphere with 15.0 ± 0.5 mg of the dried sample which was placed into an aluminum crucible (150 μL) without a lid. The furnace was heated from 30 to 900°C at the rate equal to 10°C/min. The lower heating value (LHV) of the formed gases was determined according to Tasma and Panait (2012).

**Results and discussion**

The characterization of the agro-industrial wastes before and after SLE are summarized in Table 1. Raw substrates (mainly TWR and TWG) can hold a high water content. Thus, the samples were dried to avoid steam formation during extraction and pyrolysis. In fact, during pyrolysis, the moisture content must be lower than 10% (Varma and Mondal, 2017). All materials showed high organic matter, with a VS content greater than 80%. The elemental analysis revealed that agro-wastes are rich in carbon and oxygen, while low quantities of nitrogen were detected and sulfur was below the detection limits. These compositions will prevent the formation of $NO_x$ and especially $SO_x$ during pyrolysis, both known as undesired gaseous pollutants. Total phenolic content was obtained in the liquid phase of the ethanol extraction, where WSW exhibited the highest total phenolic content extracted, with a content of 55.8 ± 5.1 mg GAE/g dry extract, followed by TWB and TWR. TWG showed the lowest content of phenolic compounds (7.0 8 ± 2.9 mg GAE/g dry extract). These results for WSW, TWR and TWB are in agreement with the literature (Silva-Beltrán et al., 2015; Pinela et al., 2017; Fontana et al., 2013).

Table 1. Characterization of tomato wastes and grape pomace before and after extraction.

| | TWR | TWRe | TWG | TWGe | TWB | TWBe | WSW | WSWe |
|---|---|---|---|---|---|---|---|---|
| TS (%) | 6.0 ± 0.5 | - | 6.4 ± 0.1 | - | 71.4 ± 1.1 | - | 76.3 ± 5.3 | - |
| VS (%TS) | 86.0 ± 0.1 | 85.6 ± 0.6 | 88.0 ± 0.1 | 91.1 ± 0.3 | 80.0 ± 0.3 | 80.8 ± 0.3 | 90.1 ± 0.4 | 90.3 ± 0.5 |
| C (%TS) | 42.0 ± 0.1 | 39.9 ± 0.2 | 38.4 ± 0.1 | 40.4 ± 0.1 | 37.3 ± 0.1 | 36.5 ± 0.1 | 48.0 ± 0.1 | 45.8 ± 0.1 |
| N (%TS) | 2.4 ± 0.1 | 3.0 ± 0.1 | 2.0 ± 0.1 | 2.4 ± 0.1 | 2.8 ± 0.1 | 2.9 ± 0.1 | 1.4 ± 0.1 | 1.6 ± 0.1 |
| O (%TS) | 35.1 ± 0.1 | 36.8 ± 0.1 | 41.7 ± 0.1 | 42.3 ± 0.1 | 34.7 ± 0.1 | 36.4 ± 0.1 | 34.6 ± 0.1 | 37.3 ± 0.1 |
| H (%TS) | 6.5 ± 0.1 | 6.1 ± 0.1 | 6.0 ± 0.1 | 6.1 ± 0.1 | 5.1 ± 0.1 | 5.0 ± 0.1 | 6.2 ± 0.1 | 5.7 ± 0.1 |
| TPh (mg GAE/ g) | 26.0 ± 1.9 | - | 7.0 ± 2.9 | - | 28.8 ± 3.0 | - | 55.8 ± 5.1 | - |

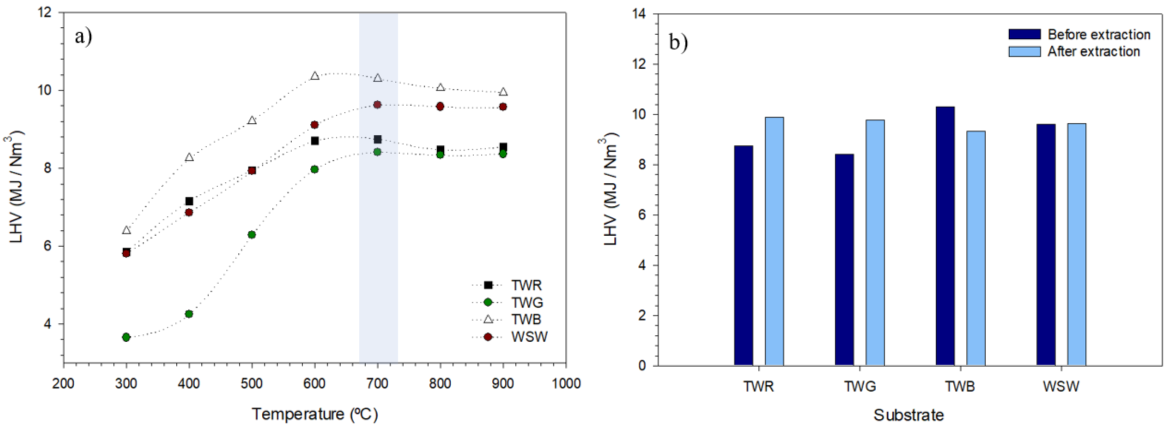

Figure 1 – LHV evaluation (a) of the gas from pyrolyzed raw materials from 300 to 900 ºC and (b) LHV obtained for agro-waste resultant gas before and after extraction at 700 ºC.

From Figure 1.a) it can be observed that all raw materials (TWR, TWG, TWB, and WSW) have the maximum LHV when the temperature approaches 700 ºC, indicating that would be the optimal temperature to produce a syngas with higher calorific value. Similar results were reported by Trasbelsi et al., (2017) for syngas production from pyrolysis of solar biosolids. It is also possible to observe that TWB and WSW pyrolysis results in a more energetic gas when compared to the other materials studied. This difference might be due to their lignocellulosic nature.

In order to evaluate the impact of phenolic compounds extraction previously to pyrolysis, LHV of the gas produced from the extracted material was determined and compared to the values obtained for the raw materials. In Figure 1.b) is possible to observe a slight increase in the LHV of syngas for TWR and TWG, whereas a slight decrease is observed for TWB. In the case of WSW no difference was observed. Globally, it is possible to state that the extraction of phenolic compounds before the pyrolysis process does not have a negative impact on the syngas quality.

This work confirmed that these agro-industrial wastes produced in high quantity are good substrates for an integrated biorefinery concept, enabling the recovery of natural phenolic compounds through extraction processes and production of high energetic syngas through pyrolytic processes.

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