Effect of storage and drying on the composition of two-phase pomace

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Introduction

The global production of olive oil in 2019-2020 reached 3.2 million tons. The European Union occupied 60% of the global production corresponding to 1.9 million tons. This production is mainly concentrated in Spain (58.4%), Italy (19.0%) and Greece (14.3%). The main production processes are three-phase and two-phase olive mills. The latter are gaining ground due to the recent legislation. Two-phase olive mills have as their product olive oil and as by-products the two-phase pomace as well as a small amount of wastewater which derives from the water used in the last stage of the clarification process (Alburquerque *et al*, 2014). The two-phase pomace is a semi-solid waste that consists of large amounts of moisture (50-75%), olive kernel, pieces of olive peel and pulp as well as residues from leaves and pruning (Christoforou *et al*, 2017). The waste of the two-phase pomace represents more than 80% of the raw material processed. Uncontrolled discharge of waste into the soil causes strong phytotoxic effects, increases soil hydrophobicity, reduces water retention and filtration rate, as well as affects acidity, salinity, nitrogen uptake, microbial activity, leaching lipid concentration, and production of organic acids and phenols (Sierra *et al*, 2007). A common valorisation pathway of the two-phase pomace is the extraction of pomace oil in pomace oil plants. A typical plant includes a drying step in a rotary drum dryer in order to reduce the moisture of pomace to 8% as well as an oil extraction step with hexane. The main environmental issue that these plants face is the emissions to the atmosphere that become a serious nuisance to the local communities. In this context, the current paper focuses on the study of the effect of storage and drying on the composition of two-phase pomace.

Materials and methods

Various samples were collected from a two-phase olive mill and a pomace oil plant in Messinia, Greece, and transferred to the Unit of Environmental Science and Technology (UEST), School of Chemical Engineering, National Technical University of Athens. Fig.1 illustrates the sampling points in the value chain of pomace oil, from the production of pomace in the olive mill until the production of dried pomace.

Fig.1. Simplified flow diagram of the sampling points in the value chain of pomace oil

Cellulose, hemicellulose, acid-soluble lignin, acid-insoluble lignin, ash and moisture were measured following the analytical procedures of NREL laboratory analytical protocols (Sluiter *et al*, 2012). Total organic carbon (TOC) and total nitrogen (TN) measured using Shimadzu's TOC-5000 series. Volatile fatty acids (VFA) were quantified by the Spectroquant Volatile Organic Acids Test kit (Merck Millipore). Ethanol, Glucose, Acetic Acid, Xylose were measured using high-performance liquid chromatography (HPLC) (0.6 mL/min, H_2SO_4 0.005M, H^+ Column). Oil was extracted using hexane as a solvent, according to the Soxhlet method, AOAC. Moreover, X-ray Powder Diffraction (XRD) analysis took place using an X-ray Bruker D8 Advance. The instrument was operated in a step-scan mode in increments of 0.02˚ 2θ, in the range of 10˚ - 50˚. The crystallinity index was calculated according to Segal (1959). In addition, Fourier-transform infrared spectroscopy (FTIR) was used as described by Moreno *et al* (1999) for the quantification of aldehydes and ketones in the oil content of the different samples.

Results and discussion

Tables 1 and 2 present the composition of the solid and liquid phases of the samples, where several differences were observed among them.

Table 1: Chemical composition of the solid phase

	Two-phase pomace	Olive pomace storage tank	Olive pomace before drying	Olive pomace after drying
Moisture, %	60.36	68.34	45.07	5.24
Total Solids, %	39.64	31.66	54.93	94.76
WSS, % d.b	15.89	14.66	12.61	20.23
Cellulose, % d.b	8.93	8.96	9.14	6.67
Hemicellulose,% d.b	27.50	29.75	27.09	20.78
AIL, % d.b	42.42	47.64	47.15	46.73
ASL, % d.b	0.94	0.90	0.99	1.56
Oil, % d.b	13.71	14.49	12.17	14.00

Table 2. Chemical composition in the liquid phase

	Two-phase pomace	Olive pomace storage tank
Conductivity, μS/cm	13680	16200
TOC, mg/L	46115	34815
TN, mg/L	96.3	91.55
VFA, mg/L	11200	14575
Phenols, mg/L	797.5	595
Xylose, g/L	3	0.05
Glucose g/L	5.05	1.5
Glycerol, g/L	1.15	-
Ethanol, g/L	9.55	12.15

Cellulose and hemicellulose showed a major decrease in concentration in the sample collected after the drying stage whilst the concentrations of these compounds remained relatively constant at the stages prior to drying. Lignin seemed to have negligible alteration during all stages. Regarding the concentrations in the liquid phase, a drop of glucose and a rise of ethanol were observed between the two-phase pomace and the sample of olive pomace storage tank, revealing the effect of storage on these soluble components and indicating that a fermentation process took place.

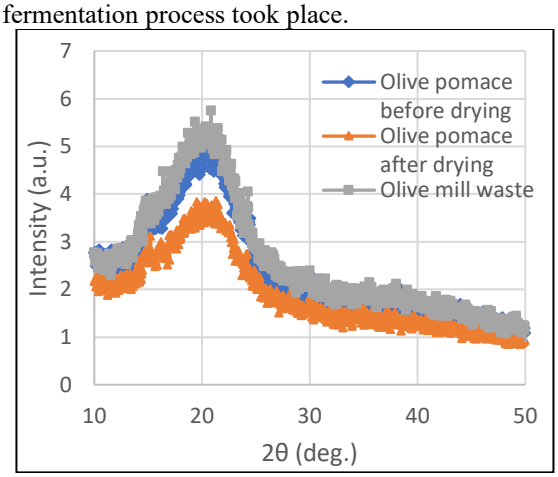

Fig. 2. XRD analysis of the examined samples

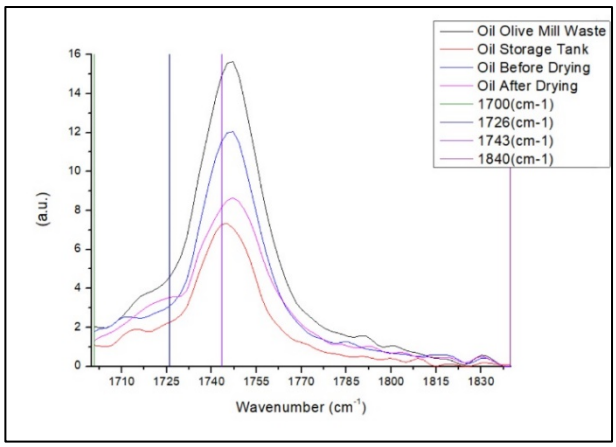

Fig. 3. FT-IR analysis of the examined samples

From the XRD analysis (Fig.2), the crystallinity indices (CI) of the samples were estimated. These results revealed that the two-phase pomace presented higher CI (CI=21.20) compared to olive pomace before (CI=16.34) and after (CI=19.70) drying. Furthermore, based on these results, it can be deduced that cellulose was converted into a more amorphous structure.

As far the FT-IR analysis is concerned, two different areas were examined. The first corresponds to the area within the range of 1700-1725 cm^{-1} which can be attributed only to the carbonyl group of aldehydes and ketones, and the area below the curve within the range 1743-1840 cm^{-1} which is attributed to the presence of fatty acid esters. It was revealed that the ratio of the prementioned areas is greater in the olive pomace storage tank sample (0.30) than in the two-phase pomace sample (0.24). That is an indication that ketones and aldehydes are produced from oil oxidation due to the presence of oxygen and UV radiation at the storage conditions. Moreover, a greater ratio of areas is observed after the drying stage (0.30) in comparison with the sample collected before drying (0.27), which may be attributed to the production of ketones and aldehydes in the drying phase due to thermal decomposition.

Conclusions

Differences in compositions have been observed in all samples of olive pomace. More specifically, the drying process seemed to have a significant effect on the decomposition of carbohydrates such as hemicellulose and cellulose. Storage conditions favoured oil oxidation and affected the oil composition. Last, the production of ketones and aldehydes is favoured in the drying phase due to thermal decomposition.

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