Journal of Thermal Analysis and Calorimetry, Vol. 94 (2008) 3, 767–771

CHARACTERIZATION AND RECOVERY OF TARTARIC ACID FROM WASTES OF WINE AND GRAPE JUICE INDUSTRIES

*D. Yalcin, O. Ozcalik, E. Altiok and O. Bayraktar**

Biochemical Engineering Research Laboratory (BERL), Department of Chemical Engineering, Izmir Institute of Technology, Gülbahçe Köyü, 35430, Urla-Izmir, Turkey

Tartaric acid is mainly used in food, pharmaceuticals and cosmetics industries. In this study, the waste samples, which contain tartaric acid, from the wastes of wine and grape juice industries were characterized by using TG, DSC, FTIR and XRD techniques. HPLC was used to determine tartaric acid content of samples. The decomposition temperatures of waste samples were found to be relatively higher compared with that of pure tartaric acid. This difference in decomposition temperatures was attributed to the presence of potassium tartrate since high potassium content was detected with ICP-AES.

Keywords: *DSC, FTIR, tartaric acid, TG, wine residues, XRD*

Introduction

Wine production industries generate a large amount of waste and by-products. Efficient, inexpensive and environmentally rational utilization of these wastes and by-products are important for higher profitability and minimal environmental impact. The valuable constituents recovered from wastes could be used in pharmaceutical, cosmetics and food industries [1]. The waste materials include vine prunings, grape stalks, grape pomace, grape seeds, yeast lees, tartrate, carbon dioxide and wastewater [2]. One of the most valuable species in these wastes is tartrate. The concentration of tartrate species was reported to be 100 to 150 kg in a tonne of wine lees and 50 to 75 kg T^{-1} grape pomace [2]. The general concentration amounts change with cultivation, climate and also wine or juice production techniques.

Although tartaric acid is a valuable product for many industries, it is an unwanted species in wine since its precipitation lowers the quality of wine. Wineries precipitate tartaric acid using calcium hydroxide or potassium hydroxide in order to obtain stable wine and then evaporate the resulting waste mixture. The obtained compact powder, which contains calcium or potassium tartrate and many other constituents (polyphenols, tannins, etc.), is sold to factories which purify tartaric acid.

In the past, farmers had a number of agricultural activities permitting them to recycle wastes and by-products from grape and wine production. Industrialized production demanded higher production volumes and the use of traditional byproducts were replaced by commercial products of low cost and high efficiency. The interest on developing product and processes for winery residues has increased and this is evident from the number of scientific publications.

In this study, the pure tartaric acid and waste samples were characterized by using TG, DSC, FTIR, XRD and ICP-AES techniques. The result from HPLC analysis was used to support findings from thermal analyses.

Experimental

Materials

The pure tartaric acid sample and waste materials were obtained from Kuzenler Import & Export Ltd. Co. (Izmir, Turkey). Other chemicals including HNO_3 (65%), Multielement solution (23 elements), HCl (32%) and H_2SO_4 (95–98%) were obtained from Merck Co. (Darmstadt, Germany). Activated carbon (powder) from Merck Co. (Darmstadt, Germany)., KOH (pellets) from Riedel-de Haen, (Seelze, Germany), Anion Exchange Resin (Dowex Marathon 11) and Cation Exchange Resin (Dowex 50WX4-100) from Sigma Aldrich Chemie (Steinheim, Germany) were used for recovery of tartaric acid.

Recovery of tartaric acid

The waste materials were dissolved in aqueous KOH solution at 80°C (pH 8). The impurities such as pigments were removed with activated carbon. Then, po-

* Author for correspondence: oguzbayraktar@iyte.edu.tr

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

tassium tartrate was precipitated by adding saturated pure tartaric acid solution. The precipitate was redissolved with acidic water at 70°C (pH 2). Cation and anion exchanges were performed in order to remove K^+ and SO_4^{2-} ions. After removing the impurities; solution was evaporated in order to obtain a saturated solution. Finally, solution was crystallized at 4°C. The obtained tartaric acid was characterized by thermal analysis.

Instrumental methods

Thermal analysis of samples was carried out by differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) (Shimadzu DSC-50) in the 25–600°C temperature range at a scan rate of 10°C min^{-1} using stainless-steel pans under nitrogen. The changes in the crystalline state were monitored by X-ray diffractometry (XRD) (Philips X'pert Pro) with CuK_α radiation for 2θ from 0 to 60°. Fourier transform infrared spectroscopy (FTIR) analysis was carried out in the spectral region of 400–4000 cm^{-1} using a FTIR spectrophotometer (Digilab FTS 3000 Mx). Elemental Analysis was performed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Varian Liberty Series Axial L 96). The HPLC equipment used was a Hewlett Packard series HP 1100 equipped with a diode array detector. The stationary phase was Aminex HPX-87H Biorad column (300×7.8 mm) thermostated at 40°C. The flow rate was 0.5 cm^3 min^{-1} and the absorbance changes were monitored at 210 nm. The mobile phase for chromatographic analysis was 5 mM H_2SO_4. External calibration was performed by using standard tartaric acid.

Results and discussion

Before applying any characterization methods, the humidity of the samples were measured for four samples including pure tartaric acid (TA), two grape juice wastes (GJW1 and GJW2) and one red wine waste (RWW). Moisture content of samples were found as 5.32, 1.75, 0.93, 0.01% for RWW, GJW1, GJW2 and pure TA, respectively.

Thermogravimetric analysis (TG)

Figure 1 showed the decomposition profiles of waste samples. There was a remarkable difference between TG curves of pure tartaric acid and waste samples. The decomposition peak for waste samples (Figs 1a, b, d) shifted to higher temperature while decomposition peak of tartaric acid was obtained at 208°C (Fig. 1c). This value matches also with the thermal decomposition temperature of pure tartaric acid reported by other researhers [3]. The first mass loss between 25 and 180°C in TG profiles of waste samples was due to water elimination. A faster mass loss was observed between 180 and 220°C, during which the organic compounds, possibly phenolics, burn. Similar observations were also made by other research groups for organic acid xerogel complexes [4].

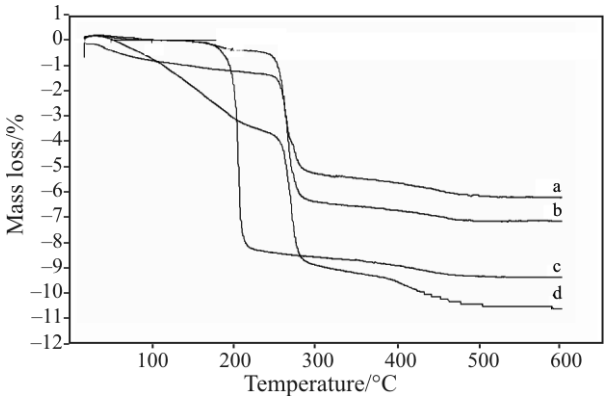

Fig. 1 TG curves of waste samples. a – GJW2, b – GJW1, c – pure TA, d – RWW

As seen from Fig. 1, decomposition peak temperatures of GJW1 and GJW2 were found to be 266 and 263°C, respectively. TG results showed that decomposition peak temperature (271°C) for RWW was little higher than those of GJW1 and GJW2. These peaks in TG profiles were possibly due to the different forms of tartaric acid. A significant shoulder around 220°C was observed for RWW (Fig. 1d). Presence of this shoulder can be attributed to decomposition of phenolic compounds in RWW.

The decomposition peak of the tartaric acid recovered from sample GJW1 was 210°C (Fig. 2a). As clearly seen from Fig. 2a, decomposition temperature of recovered tartaric acid approached the decomposition temperature of pure tartaric acid (Fig. 2c).

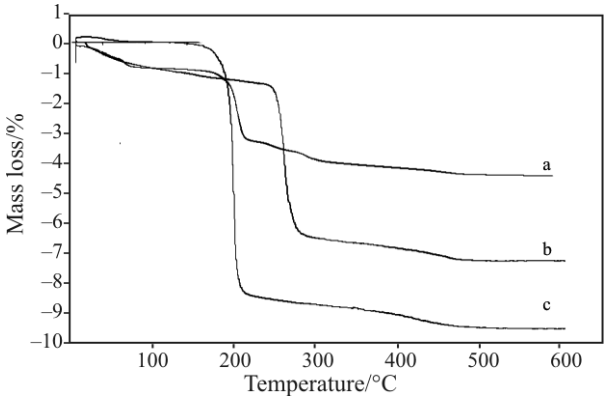

Fig. 2 TG curves of a – TA recovered from GJW1, b – GJW1, c – pure TA

Differential scanning calorimetry (DSC)

All samples showed endotherms between room temperature and 600°C. Similar to the results obtained from TG curves, the DSC curves of waste samples revealed a different endothermic character from the pure tartaric acid sample as shown in Fig. 3.

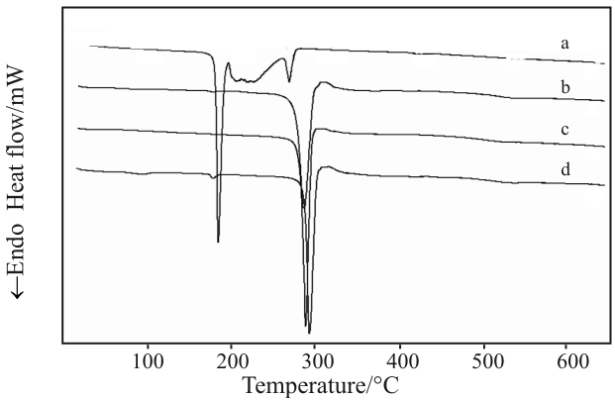

Fig. 3 DSC curves of waste samples a – pure TA, b – GJW2, c – GJW1, d – RWW

There was an endothermic melting peak at 174°C for pure tartaric acid sample. This value was in agreement with the reported melting point of tartaric acid at 170°C [5]. The remaining endotherms were due to the decomposition of phenolic compounds and tartaric acid itself as seen in Fig. 3a. As observed in TG curves, the shifting of decomposition temperatures of waste samples to higher values was due to the presence of different forms of tartaric acid which were thermally stable. Figure 3 showed that endothermic peaks for GJW1, GJW2 and RWW were obtained at 270, 269 and 274°C, respectively. In literature, differences between DSC curves of pure tartaric acid and its salt forms were also investigated [6, 7]. Results of thermal analyses revealed that salt forms of tartaric acid in waste samples were thermally more stable than the pure tartaric acid.

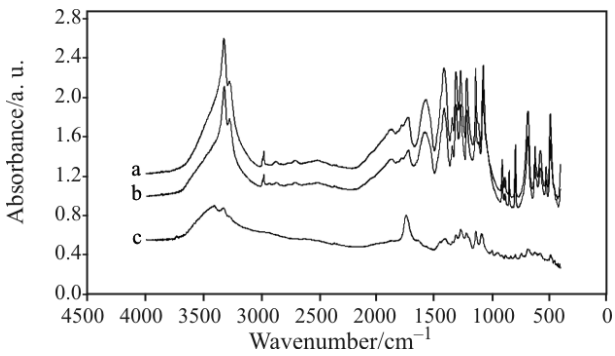

Fig. 4 FTIR spectra of waste samples a – GJW1, b – RWW, c – pure TA

Fourier transform infrared spectroscopy (FTIR)

FTIR spectroscopy was used to quantify the tartaric species in waste samples and to identify as pure sample based on the carboxylic bond (C=O).

According to Fig. 4, IR band region for tartaric acid sample was 1650–1750 cm^{-1} in good agreement with the literature values. The characteristic bands for organic acids especially tartaric and malic acids in wine were reported between 1.728–1.732 cm^{-1}. Peaks in this IR region certainly arose from stretching of the C=O bond of the carboxylic acids [8]. Also, Variankaval *et al.* found three important IR band regions for calibration of tartaric acid that were between 1500–850, 1801–1500 and 3000–2800 cm^{-1} [9].

Similarly, the C=O stretch of other waste samples occurred in the given region obtained for pure tartaric acid. The IR bands of GJW1 and RWW were 1730 and 1732 cm^{-1}, respectively. This result revealed the existence of tartaric acid in waste samples.

X-ray diffractometry (XRD)

XRD analysis was used to observe the crystallinity of pure tartaric acid and waste samples.

Diffractogram in Fig. 5 showed that some crystal structures in waste samples. The crystal structures of waste samples were similar to each other and also they were different from the crystallinity of pure tartaric acid.

Luner *et al.* [10] investigated that the effect of grinding on the crystal structure of natural tartaric acid. They concluded that there was no major difference between the crystallinity of powder and natural tartaric acid sample and also they observed the natural pattern of tartaric acid. For the 2θ range until 50°, the pattern observed by researchers were similar to the pattern given in Fig. 5d.

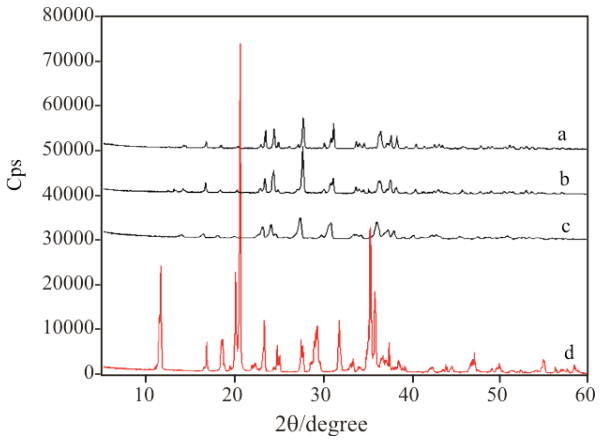

Fig. 5 XRD patterns of waste samples a – GJW2, b – RWW, c – GJW1, d – pure TA

Table 1 Concentration of elements in sample solutions prepared for ICP-AES

Sample name	Element concentration in solution (ppm)						
	Ca	Cu	Fe	K	Mg	Mn	Zn
GJW1	18.2	0.1	0.4	504.5	2.9	0.1	0.1
GJW2	10.6	0.3	0.4	518.0	0.7	0.0	0.1
RWW	85.4	0.1	0.5	504.9	0.9	0.1	0.1

High performance liquid chromatography (HPLC)

HPLC analysis was performed in order to obtain a quantative analysis of waste samples as supporting data of other characterization methods. According to the distribution curve of tartaric species, pH of the analysis media should be around 2 at which pH value most tartaric acid forms exist [11]. Therefore, in the experiments carried out, waste samples were dissolved in various HCl-water mixtures to obtain an acidic media.

The peak corresponding to pure tartaric acid having a concentration of 7.5 mg L^{-1} for 210 nm was shown in Fig. 6. Similarly, the HPLC chromatograms for waste samples showed peaks at same retention time. Tartaric acid content of GJW1, GJW2 and RWW were determined as 70, 64 and 68%, respectively.

Figure 7 showed the chromatogram of recovered tartartic acid from GJW1. The purity of this tartaric acid was determined as 97 with 3% humidity. The rest can be attributed to impurities.

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES)

All characterization results showed the presence of different forms of tartaric acid in wastes, possibly in the form of potassium or calcium tartrate. ICP-AES analyses were performed to obtain the most dominant element concentration in wastes. Analyzed elements were Ca, Cu, Fe, K, Mg, Mn and Zn. The results of analysis are tabulated in Table 1.

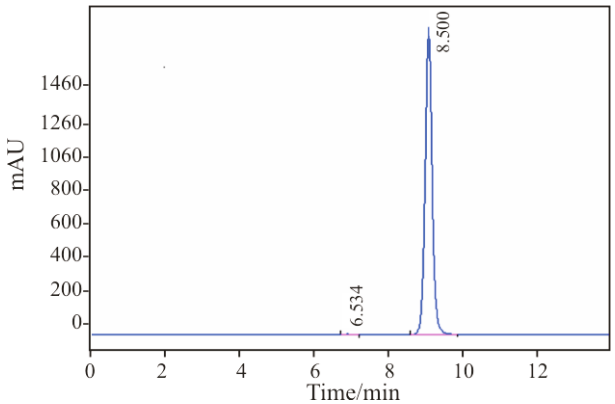

Fig. 6 HPLC chromatogram of pure tartaric acid

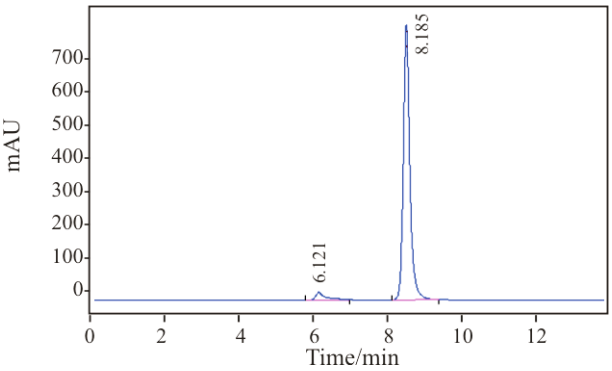

Fig. 7 Chromatogram of recovered TA from GJW1

It was shown that all samples originated from wine and grape juice production. As discussed before, tartaric acid naturally exists in grape as a constituent, and required to be removed from wine and grape juice in order to stabilize the product and to prevent future precipitations decreasing its quality. In the stabilization process, generally calcium or potassium addition is done. It was seen that concentrations of calcium and potassium were significant in the samples. Especially potassium content determined by ICP analysis was seen to be very high.

Conclusions

Thermal analysis techniques can be applicable to estimate different forms of tartaric acid in wastes from grape juice and wine indusry. Thermal analysis results showed that salt form was more thermally stable compared with pure tartaric acid. High potassium content detected by ICP-AES, revealed the presence of potassium tartrate in waste samples. Therefore, these wastes can be utilized as potential sources of natural tartaric acid.

Acknowledgements

We would like to thank to Kuzenler Export & Import Ltd. Co. for their supports.

References

1 D. P. Makris, G. Boskou and N. K. Andrikopoulos, Biores. Technol., 98 (2007) 2963.
2 E.T. Nerantzis and P. Tataridis, e-J. Sci. Tech., 1 (2006) 179.
3 D. Esquivel, J. J. Bou and S. M. Guerra, Polymer, 44 (2003) 6169.
4 N. T. Silva, C. A. Bertran, M. A. S. Oliveira and G. P. Thim, J. Non-Cryst. Solids, 304 (2002) 31.
5 F. Q. Meng, M. K. Lu, Z. H. Yang and H. Zeng, J. Therm. Anal. Cal., 52 (1998) 609.
6 R. A. Cocciardi, A. A. Ismail and J. Sedman, J. Agr. Food Chem., 54 (2006) 6475.
7 T. Vlase, G. Vlase, N. Birta and N. Doca, J. Therm. Anal. Cal., 88 (2007) 3631.
8 J. L. Moreira and L. Santos, Anal. Bioanal. Chem., 382 (2005) 421.
9 N. Variankaval, R. Wenslow, J. Murry, R. Hartman, R. Helmy, E. Kwong, S. D. Clas, C. Dalton and I. Santos, Cryst. Growth Des., 6 (2006) 690.
10 P. E. Luner and A. D. Patel, AAPS Pharm. Sci. Tech., 6 (2005) 245.
11 J S. Fritz and G. H. Schenk, Quantitative Analytical Chemistry, Allyn and Bacon, Inc., Boston 1979, p. 661.

DOI: 10.1007/s10973-008-9345-z