Biochemical Engineering Journal 116 (2016) 157–165

Contents lists available at ScienceDirect

Biochemical Engineering Journal

journal homepage: www.elsevier.com/locate/bej

Regular article

Techno-economic evaluation of wine lees refining for the production of value-added products

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ARTICLE INFO

Article history:
Received 31 January 2016
Received in revised form 7 September 2016
Accepted 9 September 2016
Available online 9 September 2016

Keywords:
Wine lees valorisation
Biorefinery
Integrated processing
Process design
Techno-economic evaluation

ABSTRACT

The cost-competitiveness of a refining process using wine lees for the production of ethanol, antioxidant-rich extract, calcium tartrate and yeast cells was evaluated in this study via process design and preliminary techno-economic evaluation. Process design was performed using the commercial process simulator UniSim (Honeywell). A sensitivity analysis was carried out to estimate the minimum selling price of the antioxidant-rich extract that should be achieved at different plant capacities in order to develop a profitable wine lees refining process. Minimum selling prices of the antioxidant-rich extract in the range of 122–11.06 $/kg are required in order to develop profitable refining schemes with wine lees processing capacities of 500 to 5000 kg/h considering 120 days of annual operating time. The final products could be used in various industrial segments including food, feed, chemical and cosmetic industries.

1. Introduction

The annual production of grapes in Europe was around 23.6 million t in 2012, out of which 90% are used for wine making [1]. Wineries produce four major by-product streams, namely grape stalks, grape pomace or mark, wine lees and wastewater. Wine lees constitute approximately 2–6% [2] of the initial grape used in wine making and therefore 0.42–1.26 million t of wine lees are generated annually in Europe. Wine lees are currently used for commercial production of calcium tartrate and ethanol [3]. The EC regulation 479/2008 revokes the EC regulation 1493/99 that necessitated the utilization of wine lees in distilleries. Holistic valorization of wine lees, as well as all by-product streams produced by wineries, should be achieved in order to develop novel products and sustainable processes in line with the requirements of bio-economy development.

Various reports have focused on the extraction of value-added products, including antioxidant-rich extracts, seed oil, fibres, tartaric acid, squalene and ethanol, from winery by-products [4–7]. Wine lees, as well as the carbohydrate fractions from grape stalks and grape marc, have been employed as fermentation media for the production of platform chemicals such as ethanol, lactic acid and xylitol [8–10]. However, winery by-product streams could be ideally employed for the separation of several value-added products. Some reports have focused on the development of novel integrated biorefineries focusing on the exploitation of the full potential of winery by-product streams [11,12]. Dimou et al. [11] produced a fermentation feedstock from the yeast cells that are contained in wine lees after the separation of antioxidants, ethanol and tartrate. The nutrient-rich hydrolysate was used for the production of 30.1 g/L of poly(3-hydroxybutyrate) using the bacterial strain *Cupriavidus necator* and crude glycerine as carbon source. Martinez et al. [12] focused on the development of a cascade refining process of red grape pomace leading to the cascade production of polyphenols by supercritical CO_2 extraction, poly(hydroxyalkanoates) from volatile fatty acids as carbon source for the cultivation of *Cupriavidus necator* and biogas via anaerobic digestion of the remaining solid stream.

The successful implementation of biorefining concepts strongly depends on sustainability issues and screening of process alternatives should be carried out based on cost-competitiveness, environmental benefits and socio-economic aspects. Process design and techno-economic evaluation of biorefining processes focusing on the production of numerous end-products from winery wastes following cascade principles should be carried out in order to assess the feasibility of process scale-up. The main aim of this work is to carry out process design and techno-economic evaluation of a wine lees refining process leading to the production of four end-products, namely ethanol, an antioxidant-rich extract,

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http://dx.doi.org/10.1016/j.bej.2016.09.004
1369-703X/

calcium tartrate and a solid fraction rich in yeast cells. The later can be used either as animal feed or for the production of fermentation nutrient supplements similar to yeast extract. Some stages of this process including the production of poly(3-hydroxybutyrate) using a hydrolysate produced from the solid fraction rich in yeast cells have been presented by Dimou et al. [11]. The effect of the unitary market price of the antioxidants-rich fraction on the overall profitability of the whole process has been evaluated in this study.

2. Materials and methods

2.1. Description of design strategy

Process design and preliminary techno-economic evaluation of the proposed biorefinery concept was carried out for processing a capacity of 500 kg/h of wine lees, which is the approximate quantity of wine lees produced from a large-scale winery in Greece [13]. The wine lees refining process was assumed to operate on a seasonal basis at 120 days (approximately 4 months) per year due to the seasonal nature of the wine making process. Thus, the biorefinery uses 1440 t/y of wine lees. The life time of the plant was set at 30 years and the interest rate at 10%. The material and energy balances were validated using the commercial process simulator UniSim (Honeywell).

2.2. Composition and fractionation of wine lees

The fractionation process evaluated in this study has been developed in lab-scale using wine lees derived from the wine making process of Merlot grape variety and were provided by the winery Ampelou Techni-Theodoros Stavrakis (Tyrnavos, Greece). The wine lees contained 62.9% (w/w) water, 5.7% (w/w) ethanol and 31.4% (w/w) solids on a dry basis (db).

The results used in the techno-economic evaluation have been obtained in lab-scale experiments using the following experimental protocols for the recovery of each component. Centrifugation is initially applied to the original wine lees for the production of liquid and solid fractions. Ethanol is recovered from the liquid fraction via distillation. The ethanol stream is subsequently used for the extraction of a phenolic-rich extract from the solid fraction at an ethanol to water ratio of 70:30 (v/v). The phenolic-rich extract constitutes 0.8% (w/w, db) of the initial wine lees. The use of ethanol was employed because it is available in the original wine lees and, therefore, the cost of the whole process can be reduced. It should be stressed that the extraction protocol of the polyphenol-rich extract has not been optimized and further work is needed in order to maximize the extraction of phenolics from wine lees.

The solids that remain after the extraction of phenolics is processed for the recovery of calcium tartrate using the methodology proposed by Rivas et al. [14]. The recovered calcium tartrate constitutes 6.5% (w/w) of the initial wine lees. The remaining solids after the separation of the phenolic-rich extract and the calcium tartrate accounts for the 24.1% of the initial wine lees. These solids contain 35% of yeast cells produced during the wine making process.

2.3. Process description and simulation

The process flow diagram (PFD) for the valorization of wine lees is shown in Fig. 1. The process was divided into three subsections, namely the recovery of ethanol, the extraction of the phenolic-rich extract and the extraction of calcium tartrate.

2.3.1. Ethanol separation via distillation

The stream of wine lees (stream 1) is fed into a solid/liquid separation unit (CF-101) where the solids are separated from the liquid. The resulting streams (solids: stream 2 and liquid: stream 3) are determined by material balances considering that the solid fraction has a content of 50% solids and 50% moisture. The liquid stream is fed to the distillation column T-101 where ethanol and water at azeotropic composition, 95% (w/w) in ethanol, is obtained as a top product stream (stream 5). The product stream of the bottom (stream 4) contains mainly water and is fed to the wastewater treatment facility.

2.3.2. Extraction of antioxidants

Stream 2 contains all solids present in the wine lees and it is mixed with the ethanol:water mixture at azeotropic composition from tank T-103, so as to achieve an ethanol to water ratio of 70:30. The combined stream is then fed to the holding and mixing tank V-101. The aim here is to use ethanol as solvent so as to extract the antioxidants present in the solids [15]. A solid/liquid separation unit (CF-102) is then used to recover most of the liquid containing the extracted antioxidants (stream 8) that is fed to a second distillation column (T-102) that operates under vacuum and produces an ethanol water mixture at azeotropic composition (stream 11) and a bottoms product (stream 10) that contains the phenolic-rich extract. A single stage evaporator (D101) is then used to remove most of the water and the concentrated antioxidant-rich stream (stream 13) is fed to the spray dryer (SD-101) where hot air is used to remove the remaining water and produce practically a moisture-free phenolic-rich fraction (stream 16).

2.3.3. Extraction of calcium tartrate

Stream 9 contains all solid components after the removal of antioxidants and is mixed with a hydrochloric acid aqueous solution (stream 17) so as the total solids are approximately 15% (w/w). The initial solid content of stream 9 was 50% (w/w). Streams 9 and 17 are fed to the holding and mixing tank V-102. In the presence of HCl, the tartrate salt (calcium tartarate), that is practically insoluble in water, is transformed to the water soluble tartaric acid according to reaction (R1).

$$CaC_4H_4O_6 + 2HCl \rightarrow C_4H_6O_6 + CaCl_2 \quad (R1)$$

Tartaric acid is recovered in stream 20 using the solid/liquid separation unit CF-103. Stream 20 is mixed with $CaCO_3$ and $CaCl_2$ to transform the water soluble tartaric acid to practically water insoluble calcium tartrate according to reaction (R2). The process used for the extraction of calcium tartrate was based on the methodology employed by Rivas et al. [14].

$$C_4H_6O_6 + CaCO_3 \rightarrow CaC_4H_4O_6 + CO_2 + H_2O \quad (R2)$$

The tartrate salt is separated from the liquid in the solid/liquid separation unit CF-104 and the solid stream (stream 24), containing 50% of solids, is fed to a spray dryer (SD-102) where moisture free solids are obtained (stream 26) using compressed hot air. The liquid stream (stream 23), that contains mostly water and ethanol, is recycled back to the distillation unit, T-101, for recovering the ethanol. The solid stream (stream 19) from the solid/liquid separation unit CF-103 contains the yeast cells which are used as either animal feed or for the production of a nutrient-rich fermentation supplement as presented by Dimou et al. [11].

2.3.4. Process design in UniSim

Fig. 2 presents the PFD of wine lees refining (Fig. 1) developed in the commercially available software UniSim Design (Honeywell). Tartaric acid and calcium tartrate were introduced to the database of UniSim. Tartaric acid ($C_4H_6O_6$, MW:150.10) has a density in aqueous solutions of 1506 kg/m^3 [16]. The heat capacity is also calculated from the same reference. Experimental and calculated values are compared in the Supplementary material (Fig. S1) as an indication of the accuracy of the process simulation. The heat of

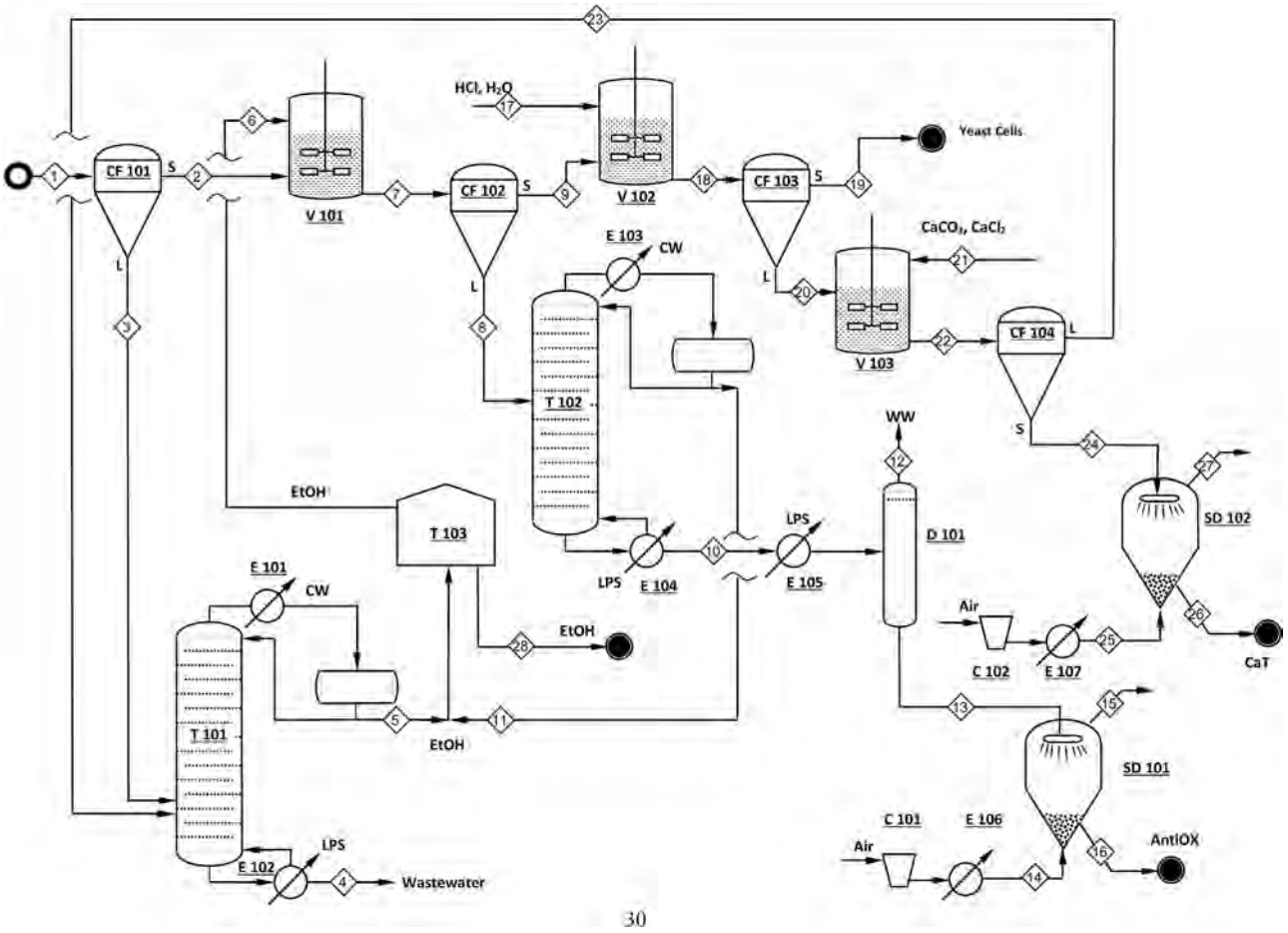

Fig. 1. Process Flow Diagram for the biorefinery process based on wine lees fractionation for the production of ethanol, antioxidant-rich.

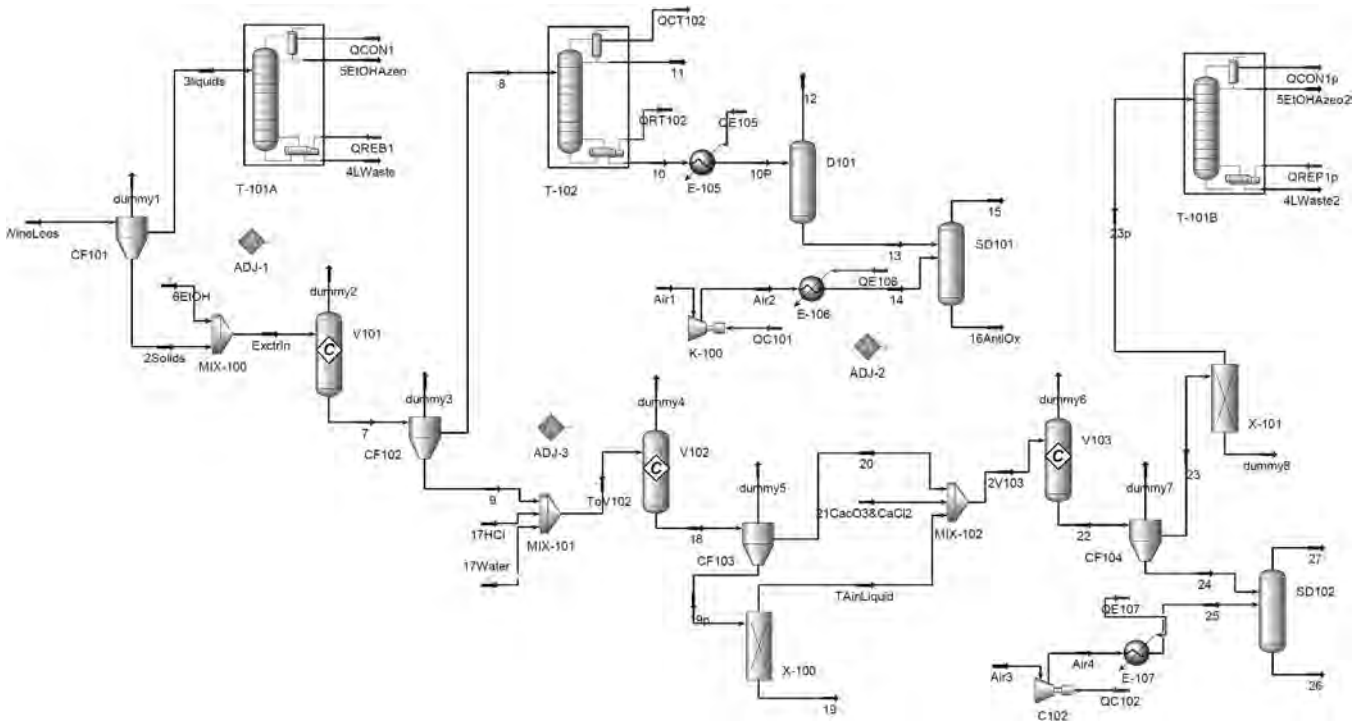

Fig. 2. Simulation model of the process shown in Fig. 1 in UniSim Design.

formation of tartaric acid given is 1,295.7 kJ/mol [17] and corresponds to the hypothetical state of undissociated tartaric acid at finite dilution. The value used for the heat of formation is validated with the calculated in UniSim Design heat of combustion (calculated: −1135 kJ/mol) which compares well with the experimental value (−1120.3 ± 0.9 kJ/mol) also given in the same reference. Data for calcium carbonate and calcium chloride are taken from [18]. The heat of formation of calcium carbonate and calcium chloride are 1220 kJ/mol and 877.1 kJ/mol, respectively. The NRTL/PR thermodynamic model is used to simulate the process under study.

The material and energy balances of representative streams of the process flow diagram presented in Fig. 1 are provided as Supplementary material in Table S1.

2.4. Estimation of the fixed capital investment

Based on the process flow diagram presented in Fig. 1 and the material and energy balances estimated and validated in UniSim, the equipment type was selected and the characteristics of each equipment were determined based on standard engineering procedures and rules of thumb for the design and sizing of process equipment [19–23]. The equipment purchase cost (C_P) was used for the estimation of the fixed capital investment (FCI) using the equation $FCI \approx 5 \times C_P$. This equation was used because it has been proposed [19,21] that the FCI can be estimated using the equipment purchase cost and a multiplier in the range 3–6. When the sizing of equipment has been completed then data from the textbooks of Peters et al. [19] and Green and Perry [23] were used in combination with Eq. (1)

$$C_p = \frac{CEPCI_t}{CEPCI_{t0}} C_{p,0} \left(\frac{X}{X_0} \right)^n \quad (1)$$

where $C_{p,0}$ is the purchase cost of a particular type of equipment at year t_0 with characteristic size X_0, C_p is the purchase cost of the same type of equipment in 2013 with the determined characteristic size X as was estimated in this study, n is the exponent that is characteristic to the particular type of equipment and $CEPCI_t$ is the chemical engineering plant cost index at year t published monthly in the Chemical Engineering magazine.

2.5. Estimation of the cost of manufacture

The cost of manufacture without depreciation is calculated based on Eq. (2) [21] that includes the FCI, the cost of utilities (C_{UT}), the cost of raw materials (C_{RM}), the cost of operating labor (C_{OL}) and the cost of wastewater treatment (C_{WT}).

$$COM_{woD} = 1023(C_{RM} + C_{UT} + C_{WT}) + 2.73C_{OL} + 0.18FCI \quad (2)$$

The utility requirements (electricity, low pressure stream and cooling water) are determined based on the material and energy balances and their cost (C_{UT}) is then calculated. To determine the operating labor cost (C_{OL}), the workers necessary for each equipment unit per shift are initially estimated and then the overall number of workers necessary for the operation of the plant are determined. The cost of raw materials (C_{RM}) is calculated based on the unit price of each feedstock used and the annual consumed amount. The cost of the waste treatment (C_{WT}) for wastes produced from unit operations were determined by considering that the cost per t of non-toxic wastes was 50 $ [21].

2.6. Estimation of the product minimum selling price

To assess the feasibility and viability of the proposed process for wine lees valorization the potential revenues must be calculated and the cash flows must be assessed. This is necessary in order to estimate several economic indices such as the net present value and the payback period. Discounted cash flow (DCF) analysis was carried out in order to determine the conditions under which the proposed process for wine lees valorization is viable. The DCF focus on the calculation of the selling price, in $/kg, of a product for which the net present value (NPV) is zero. This selling price is defined as the minimum selling price (MSP) of the product. The DCF analysis was carried out according to the assumptions presented in the 2011 NREL bioethanol production report [22]. According to this report, the assumptions followed include a 10% discount rate (or internal rate of return), 30 years of plant lifetime, 100% of equity financing, 7 years depreciation based on the Modified Accelerated Cost Recovery System (MACRS), 35% of corporate tax rate, 3 years duration of plant construction, working capital 5% of FCI and zero salvage value for equipment and land. During the construction period, it is considered that the distribution of plant construction costs is 8%, 60% and 32% for the 1st, 2nd and 3rd year of the plant construction period, respectively.

In order to determine the MSP at different plant capacities, the raw material cost, the utilities cost, the waste treatment cost and revenues are scaled linearly with the amount of wine lees processed. The FCI is determined analytically and it was observed that it scales approximately according to the following equation:

$$FCI = FCI_0 \left(\frac{WL}{WL_0} \right)^{0.534} \quad (3)$$

where FCI_0 is the fixed capital investment for processing of 500 kg/h of wine lees (this is starting wine lees capacity processed, WL_0) and WL is the amount of wine lees processed in kg/h.

The cost of operating labor is scaled according to the following empirical equation [23]

$$C_{OL} = C_{OL,0} \left(\frac{WL}{WL_0} \right)^{3/4} \quad (4)$$

where $C_{OL,0}$ is the labor cost for processing of 500 kg/h of wine lees.

2.7. Analysis of total polyphenolic concentration

The Folin-Ciocalteu assay was employed for the determination of the total polyphenol concentration using the methodology reported by Arnous et al. [24]. The protocol started by vortexing a mixture of 0.02 mL of sample, 0.78 mL of distilled water and 0.05 mL of Folin-Ciocalteu reagent. An aqueous solution of 20% (w/v) sodium carbonate was added to the aforementioned mixture after 1 min followed by vortexing of the mixture, which remained in the dark for 60 min at room temperature. The total polyphenol concentration was estimated at 750 nm using a calibration curve (50–700 mg/L) with gallic acid as a standard. The total polyphenol content was expressed as g gallic acid equivalents per g of dry wine lees using average values of triplicates for each sample.

3. Results and discussion

3.1. Estimation of purchase equipment cost and FCI

Table 1 presents the purchase cost of each unit operation and the FCI of the process presented in Fig. 1. The calculations were based on the processing of 500 kg/h of wine lees. The unit operations that contribute the highest cost to the total purchase equipment cost are the four centrifugation units that cost $87,000 each. In addition, the distillation columns T-101 and T-102 with 22 and 20 sieve plates, respectively, contribute a total purchase cost of $119,100. The total purchased equipment cost was estimated to be M$ 0.776 and this led to a fixed capital investment of M$ 3.879.

Table 1
Estimation of purchase equipment cost and fixed capital investment.

Unit		Characteristics	Data source	Purchase Cost (k$ 2013)
CF101	Disc Centrifuge	D = 9 in, motor size of 20 hp (14.9 kW), it can be used at flow rates up to 9 m^3/h	[23]	87.0
T101	Distillation Column	H = 14.9 m, D = 0.35 m, 22 sieve plates	[19]	49.7
E101	Heat Exchanger	Double pipe, A = 3.38 m^2	[19]	3.0
E102	Heat Exchanger	Double pipe, A = 3.95 m^2	[19]	3.1
V101	Mixing tank	Glass lined, V = 2.6 m^3, working volume 50%	[19]	86.2
CF102	Disc Centrifuge	D = 9 in, 20 hp motor	[23]	87.0
T102	Distillation column	H = 13.5 m, D = 0.85 m, 20 sieve plates	[19]	69.4
E103	Heat Exchanger	Shell & tube, A = 19.2 m^2	[19]	3.5
E104	Heat Exchanger	Reboiler, A = 19.3 m^2	[19]	3.5
E105	Heat Exchanger	Double pipe, A = 1.15 m^2	[19]	2.8
D101	Drum	H = 0.7 m, D = 0.23 m	[19]	4.3
C101	Blower	0.1 m^3 air/s, 3 psi max discharge	[19]	6.5
E106	Heat Exchanger	Air Preheat, CS, A = 1.62 m^2	[19]	3.0
SD101	Spray Dryer	Max evap. rate 0.03 kg H_2O/s	[19]	27.3
V102	Mixing Tank	Glass lined,V = 1.2 m^3, working volume 50%	[19]	54.5
CF103	Disc Centrifuge	D = 9 in, 20 hp motor	[23]	87.0
V103	Mixing tank	Glass lined, V = 0.9 m^3, working volume 50%	[19]	46.0
CF104	Disc Centrifuge	D = 9 in, 20 hp motor	[23]	87.0
C102	Blower	0.3 m^3 dry air/s, 3 psi max discharge	[19]	13.2
E107	Heat Exchanger	Air Preheat, CS, A = 0.54 m^2	[19]	2.0
SD102	Spray Dryer	Max evap. rate 0.03 kg H_2O/s	[19]	27.3
T103	EtOH Storage Tank	CS Shop Fabricated tanks 20 m^3	[19]	22.5
TOTAL PURCHASE EQUIPMENT COST (M$)				0.776
FIXED CAPITAL INVESTMENT (M$)				3.879

Table 2
Consumption and cost calculation of utilities requirements.

Unit operation	Electricity (kWh/y)	Low pressure steam (t/y)	Cooling water (t/y)
CF101	42,910		
V101	3,745		
CF102	42,910		
C101	5850		
V102	1,730		
CF103	42,910		
V103	1,270		
CF104	42,910		
C102	2880		
E102		1180	
E104		5,752	
E105		343	
E106		57	
E107		19	
E101			48,400
E103			274,830
TOTAL	187,115	7,351	323,230
Unit Price	0.06 $/kWh	12 $/t	0.015 $/t
Total Cost ($/y)	11,230	88,212	4850
UTILITIES COST (M$/y)			0.105

3.2. Estimation of the utilities cost

Table 2 presents the utilities required per unit operation as well as the total utilities cost for processing 500 kg/h of wine lees. Specific unit operations, such as the mixing tanks and centrifugation units, require electricity, while other unit operations, such as heat exchangers, require low pressure steam (heaters) or cooling water (coolers). The unit prices of the electricity, low pressure steam and cooling water were set to 0.06 $/kWh, 12 $/t and 0.015 $/t according to Turton et al. [21]. Approximately 84.6% of the utilities cost is due to steam requirements and specifically to the E-104 boiler of the distillation column T-102 (5752 t/y), where water and antioxidants are separated from the ethanol water mixture at azeotropic composition. The utilities cost was estimated at 0.105 million $ per year.

3.3. Estimation of labor cost

The labor cost was calculated according to the number of workers needed per shift multiplied by 4.5 and the annual average salary of workers which is equal to 35,000 $ [22]. In this process, due to the seasonal operation of the plant, salaries are accounted only for 120 days (approximately 4 months) per year resulting in a C_{OL} equal to 0.093 million$ per year.

3.4. Estimation of the cost of raw materials

The unit price of raw materials, the annual cost of raw materials and their annual consumption are presented in Table 3. The total cost of raw materials is lower (0.064 million $ per year) than the C_{OL} and C_{UT} mainly due to the low processing capacity of the plant and the low purchase price of wine lees (0.01 $/kg).

Table 3
Raw materials consumption and cost calculation summary.

Raw Material	Consumption (kg/h)	Consumption (t/y)	Unit Price [a] ($/kg)	Cost (M$/y)
Wine Lees	500.00	1440.00	0.01	0.015
HCl 37%	55.45	159.70	0.22	0.035
$CaCO_3$	15.79	45.48	0.15	0.007
$CaCl_2$	15.79	45.48	0.15	0.007
TOTAL RAW MATERIALS COST (M$/y)				0.064

[a] [25].

3.5. Estimation of the wastewater treatment cost

Another cost contributing to the total manufacturing cost is the cost of the wastewater treatment (C_{WT}). Liquid wastes are mainly produced from the bottom of the distillation column T-101 (stream 4 in Fig. 1), but also from the evaporator D-101 (stream 12 in Fig. 1). The above waste streams account for 169.7 kg/h from stream 4 and 110 kg/h from stream 12 and lead to an annual cost for waste treatment of 0.04 million $ per year.

3.6. Estimation of the cost of manufacture

The cost of manufacture is calculated by Eq. (1) as M$ 1.21 in the case that 500 kg/h of wine lees are processed in the proposed biorefinery concept. Table 4 present the total capacity of end-products fractionated from wine lees and the associated revenues. It is important to note that for the three commodity products (namely ethanol, calcium tartrate and yeast cells) the selling prices do not vary significantly and the values used in this study are representative for these end-products. Calcium tartrate is mainly used in the food industry. Ethanol from wine lees is used as potable ethanol or alternatively could be used in several applications, such as platform chemical. However, the market price of the antioxidants may vary significantly depending on their purity, the origin and the final application.

Tao et al. [26] optimized the extraction of total phenolics from wine lees (58.76 mg of gallic acid equivalents per g of dried wine lees) via ultrasound-assisted extraction using aqueous ethanol solution of 43.9% ethanol. Wu et al. [27] reported the extraction of 24.1% of total polyphenols using an ethanol:water mixture with 95% ethanol content and a soxhlet extractor. In the studies of Tao et al. [26] and Wu et al. [27] the composition of phenolics in the extract was not identified. Perez-Serradilla and Luque de Castro [28] carried out microwave-assisted extraction of phenolics from the dried solid phase of wine lees that was separated from the liquid phase via centrifugation. An acidified ethanol:water mixture of 75% (v/v) ethanol was used as extraction solvent. The dried phenolic-rich extract contained 364 mg of gallic acid equivalents per g of wine lees extract powder with an antioxidant activity of 3930 μmol of Trolox equivalents per g of wine lees extract powder. The main phenolics in the dried extract were p-coumaroyl derivatives, quercetin, quercetin-3-β-glucoside, myricetin, p-coumaric acid and caffeic acid [28]. Delgado de la Torre et al. [29] reported that the extracts obtained from wine lees by ethanol water mixtures and microwave-assisted extraction were rich in numerous compounds such as primary amino acids, anthocyans, flavanols, flavonols, flavones and non-flavonoid phenolic compounds, among others. Varying efficiencies on the extraction of phenolic compounds from wine lees can be achieved by different technologies such as solid-liquid extraction, grinding, soxhlet extraction, microwave-assisted extraction, ultrasound-assisted extraction, high pressure extraction, pulsed electric fields extraction and supercritical fluid extraction [26,27,30].

In this study, an ethanol:water mixture with 70% ethanol has been used as the solvent system for the extraction of polyphenols from the solid fraction of wine lees. The proposed process exploits the ethanol content in wine lees, which can be exploited for the extraction of antioxidants from the same raw material. In this way, the simultaneous production of a value-added product (potable ethanol) and extraction of antioxidants using recycling of ethanol can be achieved. It should be stressed that the extraction of polyphenols from the solid fraction of wine lees has not been optimized. The total polyphenol content determined by the Folin-Ciocalteu assay in this study was 26.1 mg of gallic acid equivalents per g of dry wine lees, which is lower that the respective values reported by Tao et al. [26] and Perez-Serradilla and Luque de Castro [28], namely 58.76 mg of gallic acid equivalents per g of dried wine lees and 364 mg of gallic acid equivalents per g of wine lees extract powder, respectively. However, the optimization of polyphenol extraction from wine lees involves the comparison of different extraction technologies, such as ultrasound or microwave assisted extraction among others [30]. In this study, the profitability margin of the proposed wine lees refining process has been presented using a simple solid-liquid extraction system. The development of a polyphenol-rich extract with higher polyphenol content and extraction yield together with cost estimation of the optimized system and the identification of market outlets should be the focus of future studies. Polyphenol-rich extracts from winery wastes and by-products of varying purities could be used as additives for food and cosmetic applications [30].

3.7. Calculation of the MSP of antioxidants for different wine lees processing capacities

Due to the fact that it is difficult to estimate a market price of the antioxidant-rich fraction, the profitability of the plant processing the wine lees will depend on the revenue achieved from the antioxidant-rich fraction. The approach followed in this study was based on the calculation of the MSP of the antioxidants-rich fraction (that result in zero NPV at the end of the lifetime of the industrial facility) as a function of the amount of the processed wine lees. For each capacity of processed wine lees, the NPV was assessed using the COM, FCI and C_{OL} values estimated using Equations (2), (3) and (4), respectively.

The results of the DCF analysis are presented in Fig. 3. The MSP of the antioxidants-rich fraction is 122 $/kg when 500 kg/h of wine lees are processed but decreases significantly when the amount of wine lees processed is increased ten times (i.e. when 5000 kg/h of wine lees are processed) where the MSP becomes 11.06 $/kg. In order to assess the potential implementation of the proposed process, the wine production capacities in Southern European countries could be taken into consideration [1]. The utilization of grapes for wine making in Greece, Italy, France and Spain in 2012 was 0.68, 4.65, 5.28 and 4.97 Mt, respectively. Taking into consideration that an average of 4% of wine lees is produced as related to the grape capacity used in wine making, then the annual wine lees production in Greece, Italy, France and Spain could be estimated as 27,000 t, 186,000 t, 211,000 t and 199,000 t, respectively. The techno-economic evaluation was carried out considering that the plant operates for 2880 h per year processing 14,400 t wine

Table 4
Annual capacity of end-products and associated revenues.

Material	Production (kg/h)	Recovery (%)	Production (t/y)	Unit Price ($/kg)	Revenues (M$/y)
EtOH	14.11	49.51	40.63	0.6[a]	0.025
Antioxidants	3.39	84.75	9.76	*x*	0.00976 *x*
Calcium tartrate (FOOD GRADE)	29.25	90.00	84.24	5.0[a]	0.421
Yeast cells for animal feed	120.50	100.00	347.04	1.0[a]	0.347
TOTAL REVENUES (M$/y)					0.793 + 0.00976*x*

[a] [25].

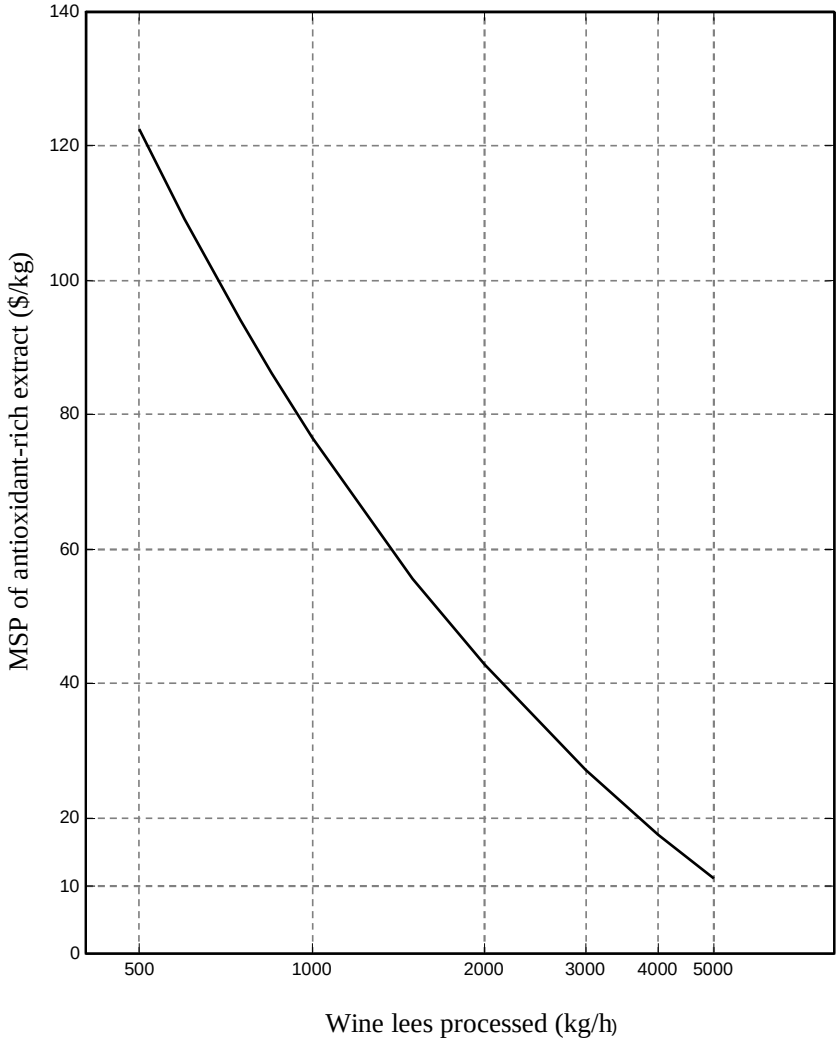

Fig. 3. Minimum selling price of antioxidants-rich fraction as a function of the amount of wine lees processed.

lees per year. According to the sensitivity analysis carried out in this study (Fig. 3), the proposed wine lees refining concept could be implemented in major wine producing countries, such as Italy, Spain and France.

The yeast cells produced in the proposed biorefinery concept could be used as animal feed, the extraction of value-added components in yeast cells or the production of a nutrient-rich fermentation supplement equivalent to yeast extract. Value-added components, such as β-glucan and mannoprotein compexes [31,32], could be also extracted from yeast cell walls increasing the final products derived from the proposed biorefinery concept leading to further diversification of market outlets. Dimou et al. [11] optimized a process for the production of nutrient-rich supplements that were employed successfully for the production of poly(3-hydroxybutyrate). Lin et al. [33] has proposed the utilization of similar wine lees derived hydrolysates for the production of microbial oil using oleaginous yeasts. The utilization of such complex sources of nutrients from industrial waste and by-product streams would be essential in order to enhance the fermentation efficiency of fastidious microorganisms, such as the production of succinic acid by *Actinobacillus succinogenes* and lactic acid by *Lactobacillus* strains. Perez-Bibbins et al. [25] presented the potential exploitation of lees from wine, beer and cider production processes for sustainable generation of yeast extract via autolysis or cell disruption. Such yeast extracts could be also produced via acid hydrolysis of yeast cells.

The MSP of antioxidant-rich extracts estimated in this study was in the range of 11.06–122 $/kg, which is within the range of the market price (10–100 $/kg or higher depending on the purity and the active compounds contained in the extract) of antioxidant-

rich extracts isolated from grapes [34]. The market prices of assai extract powder vary in the range of 9.5–25 $/kg [35]. The extraction of antioxidant-rich extracts from various renewable raw materials has been estimated in literature-cited publications. The COM of crude extracts recovered from jussara pulp were estimated in the range of 87.32–167.48 $/kg [35]. Farias-Campomanes et al. [36] reported that the extraction of phenolics using grape bagasse from Pisco residues by supercritical CO_2 will result in a COM of 133.16 $/kg considering a plant capacity of 0.5 m^3 with an expected phenolic content of 23 g/kg of extract. Furthermore, the process used for the extraction of antioxidant-rich fractions is crucial in order to reduce the COM as reported by Santos et al. [37] for the extraction of three fractions rich in bioactive compounds (i.e. crude fraction, anthocyanin-rich fraction and fraction rich in phenolic compounds) via pressurized liquid extraction or low pressure solvent extraction using jabuticaba skins. The pressurized liquid extraction process resulted in 40-fold reduced COM for producing fractions of similar recovery yields as was achieved by the low pressure solvent extraction method. The cost of manufacture of different antioxidant-rich extracts reported in the literature, the market prices of antioxidant-rich extracts and the MSP of antioxidant-rich extracts achieved in this study show that the development of biorefinery concepts for the extraction of antioxidant-rich extracts as well as other value-added products could lead to the implementation of cost-competitive processes.

It should be stressed that if the extraction yield and the purity of the final antioxidant-rich extract is further increased then higher market prices could be achieved, thus improving the profitability of the whole process. However, the cost of manufacture of extracts recovered by different extraction methods should be estimated in order to evaluate the cost-competitiveness of the advanced process.

4. Conclusions

This study presented the economic potential for the development of a biorefinery based on wine lees valorization leading to the production of antioxidant-rich extract, calcium tartrate, ethanol and yeast cells. The sensitivity analysis showed the plant capacities required in order to develop cost-competitive processes depending on the MSP of antioxidant-rich extracts. The holistic utilization of all winery by-products, grape stalks, grape pomace and wine lees, could lead to the development of integrated biorefineries for the production of many products with diversified market outlets.

Acknowledgments

This work is part of the “Valorization of cheese dairy and winery wastes for the production of high added-value products” project (19SMEs2009), implemented within the National Strategic Reference Framework (NSRF) 2007–2013 and co-financed by National (Greek Ministry—General Secretariat of Research and Technology) and Community Funds (E.U.—European Social Fund). This work is also included in the Cost Action TD1203 entitled “Food waste valorisation for sustainable chemicals, materials & fuels (EUBis)”.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.bej.2016.09.004.

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