

Review

Thermal and Non-Thermal Physical Methods for Improving Polyphenol Extraction in Red Winemaking

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Abstract: Maceration-fermentation is a critical stage in the elaboration of high-quality red wine. During this stage, the solid parts of the grape berries remain in contact with the fermenting must in order to extract polyphenols mainly located in the grape skin cells. Extracted polyphenols have a considerable impact on sensory properties (color, flavor, astringency, and bitterness) and on the aging behavior of red wine. In order to obtain wines with a sufficient proportion of those compounds, long maceration times are required. The presence of the solid parts of the grapes during red wine fermentation involves several problems for the wineries such as production capacity reduction, higher energy consumption for controlling the fermentation temperature and labor and energy consumption for periodically pump the grape must over the skin mass. Physical techniques based on heating such as thermovinification and flash expansion are currently being applied in wineries to improve the extraction of polyphenols and to reduce maceration time. However, these techniques present a series of problems derived from the heating of the grapes that affect wine quality. A series of recent studies have demonstrated that non-thermal innovative technologies such as pulsed electric fields (PEF) and ultrasound may represent effective alternatives to heating for assisting polyphenol extraction. In terms of general product quality and energetic requirements, this review compares these thermal and non-thermal physical technologies that aim to reduce maceration time.

Keywords: red wine; thermovinification; flash-release; pulsed electric fields; ultrasound

1. Introduction

Red wine is obtained from the must of red grapes that undergoes fermentation together with the solid parts of the grape berries. In this step, known as maceration-fermentation, sugars of the must are converted into ethanol by yeast, and polyphenolic compounds are extracted mainly from the grape skin and the seeds.

Maceration-fermentation is the most critical stage in the red winemaking process. It is essential for obtaining high quality red wines, but is also the one that requires the most energy and workforce. It is estimated that about 64.3% of the total energy needed to produce a liter of wine is consumed during the maceration-fermentation stage [1]. Polyphenols are key actors in red wine, since they are involved in its sensory properties (color, flavor, astringency, and bitterness) [2], in its aging behavior, and in beneficial health effects attributed to moderate wine consumption [3]. In traditional red winemaking, in order to obtain a final product with high polyphenol content, the solid parts of the grape pomace remain in contact with the must during the entire alcoholic fermentation process (7–10 days), or even over a longer period of time. Although maximum anthocyanin content and color intensity is already achieved during the first days of maceration [4,5], the extraction of procyanidins and other flavonoids,

which have significant impact on other sensory attributes such as astringency and mouthfeel, requires longer maceration periods [6,7]. As these compounds are mainly located in the seeds, its extraction required the presence of ethanol to disorganize the outer lipidic cuticle surrounding the seeds [8]. On the other hand, in red winemaking: aromatic precursors responsible for the varietal aromas in wines are extracted from the solid parts of grape barriers, along with polyphenolic compounds.

The necessity of maintaining the solid parts of the grape berries in contact with the fermenting must leads to several issues faced by wineries in the red winemaking process [9]. It is estimated that approximately 20% of the fermentation tanks are occupied by the solid parts, resulting in a reduction of the effective volume of the tanks and, as a consequence, of a winery's production capacity. This issue becomes especially significant at the peak of harvesting, when the fermentation-maceration tanks' production capacity may be exceeded. Other negative side effects of longer maceration periods are related with the difficulty of controlling the temperature increment as a consequence of the fermenting activity of the yeasts when the solid parts are present in the fermentation tanks, as well as with the labor force and energy consumption required to periodically pump the wine over the skin mass that rises to the top of the fermentation tanks [10].

Different strategies have been adopted in wineries to enhance the extraction of phenolic compounds and to reduce the duration of the maceration-fermentation stage in red winemaking [11,12]. Physical technologies based on heating, such as thermovinification and flash expansion, are currently being applied in wineries for this purpose [13]. They present a series of problem such as the difficulty involved in stabilizing the color, the loss of varietal aromas through temperature increment, and the consumption of high quantities of energy [14,15]. A series of studies have recently demonstrated that non-thermal innovative technologies such as pulsed electric fields and ultrasound may represent effective alternatives to heating in the attempt to improve polyphenol extraction [16–19]. This review compares thermal and non-thermal physical technologies that aim to reduce maceration time in terms of equipment complexity, energetic requirements, and overall quality of the red wine.

2. Thermal Technologies for Improving Polyphenol Extraction

Although the heating of red grapes in order to reduce maceration has been investigated since the early 20th century, the process was not commercially adopted until the 1970s, when industrial heating systems were developed for that purpose [20].

In general terms, the process consists in heating grapes to over 70 °C for a period of time ranging from a few minutes to several hours. As a consequence of heating, the cell envelopes of the grape skins are braked down, thereby facilitating the subsequent release of polyphenols (mainly anthocyanins) that are located inside the cells into the liquid phase [21]. Heating also denatures enzymes such as polyphenol oxidase, thereby preventing browning. In fact, heating was originally used to prevent laccase activity in grapes contaminated with the mold *Botrytis cinerea* [22].

Although generally heating of the grapes before fermentation is called "thermovinification", different pre-fermentation heating processes are currently being applied in wineries. These techniques can be classified into two groups, depending on whether the cooling of the grapes, similarly to heating, is conducted using heat exchangers, or whether the cooling is conducted into a vacuum chamber. The first kind of process is designated as "thermovinification", along with its variations, known as "pre-fermentation hot maceration" (MPC), and "short-time-high-temperature treatment with warm maceration" (KZHE). The second group involves the technique called thermo-flash, flash détente or flash-release.

2.1. Thermovinification, MPC, and KZHE

2.1.1. Description of the Techniques

Thermovinification, MPC, and KZHE are pre-fermentative heating techniques; they all have in common that the temperature of the grape mash does not increase above 85 °C, and that heating and cooling are conducted in heat exchangers [23].

In thermovinification, heating up to around 70 °C is conducted for a period of time of less than one hour, after which the grape mash is pressed to separate the solid parts and perform fermentation as for white wine. If heating at the same temperature is extended for a longer period of time (up to 24 h), and the fermentation is conducted in the presence or absence of the solid phase, the process is called MPC (“pre-fermentation hot maceration”). A variation of MPC is the process developed in Germany called KZHE (“short-time-high-temperature treatment with warm maceration”). In the latter, fermentation is conducted in the absence of solids after maintaining the grapes at around 45 °C for 6–10 h after having heated them to around 85 °C for 2 min.

2.1.2. Equipment

The simplest and most inexpensive heat exchangers used to heat grapes before fermentation are tube-in-tube heat exchangers. To prevent blocking problems in this heat exchangers, it is required the application of the treatment to the entire mix of juice and solid parts. To save energy, it is recommended to treat the solid parts after pre-draining in order to minimize the quantity of material that needs to be heated and cooled. In this case, it is recommended to use a scraped-surface heat exchanger with a rotating shaft that improves heat transfer to the product. This approach permits to process the grape mash with a moderate degree of pre-draining while avoiding blocking issues.

Different approaches have been developed to save energy in the heating of the grape mash by recovering heat. In such systems, incoming well-mixed crushed grapes without any pre-draining are pre-heated together with the crushed grapes that have already been heated. In these systems, and in order to avoid blocking, spiral heat exchangers or heat exchangers with a section of rectangular or parallel rectangular channels are preferred.

An alternative to the above-described continuous single pass method is to heat the grape mash with a tube-in-tube heat exchanger while recirculating them on a tank. This approach, generally used in smaller wineries, results in slower and more heterogeneous heating.

For transformation the sugar of must into ethanol by yeasts during fermentation, temperatures between 20 and 30 °C are required. Therefore, after the heating period, it is necessary to cool down the grape mass prior to fermentation. The cooling step is conducted with heat exchangers similar to those that are used for heating.

Fluids used in this type of equipment are hot water or steam for heating, and cold water or glycol for cooling.

In general, such installations used for pre-fermentative heating occupy a considerable area within the winery. The space is required for the heat exchanger systems as well as for the facilities designed to heat and cool the fluids.

2.1.3. Impact of the Treatment in the Composition of Wine

The main objective in using these pre-fermentation heating techniques is to speed up the extraction of polyphenols from the grape skins with the purpose of eliminating or reducing the maceration stage. However, the characteristics of the final wine obtained with such heated grapes may be affected [24,25].

As a consequence of heating, wild yeast populations are inactivated, thus requiring the addition of microbial starters to trigger fermentation. Generally, alcoholic fermentation is initiated without problems after pre-fermentation heating. Occasionally a more abrupt fermentation than in traditional fermentation is observed, probably related to the release of nutrients from the solid parts of the grapes as a consequence of heating [26]. A significant increase in sugar concentration, pH, amino acids, and

ammonium in thermovinified Carignan must was reported [27]. Bacterial populations of lactic as well as acetic bacteria are also inactivated, resulting in wines with low volatile acid content. Total acidity of wine is not usually affected by pre-fermentation heating. Although a more elevated extraction of cations and anions as a consequence of grape heating has been described, they precipitate as salts of tartaric acid, thus ultimately leaving wines thus obtained in the same condition as untreated wines [28].

Pre-fermentation heating, in which the solid parts of the grapes are pressed and fermentation is conducted in the liquid phase, has the main objective of enhancing the extraction of color from the skins. The color increment is a consequence of the rapid extraction of anthocyanins.

While anthocyanins are extracted since the first moments of fermentation, flavanols require the presence of ethanol to be extracted.

Piccardo and González-Neves [29] reported that the extraction of anthocyanins after thermovinification was practically immediate. As consequence the anthocyanin concentration and the color intensity in the first days of fermentation were 21% and 45% higher, respectively, than in control. Most studies of the thermovinification technique have been conducted with Pinot noir due to the difficulty of extracting anthocyanins from that grape variety. It has been reported that the anthocyanin quantity in the Pinot noir variety reached a maximum at the onset of fermentation, with a concentration 2 to 3 times higher than in traditional fermentation. A drastic decrease in anthocyanins was observed, however, towards the end of fermentation [30]. Studies conducted at laboratory scale have demonstrated the degradation of anthocyanins due to temperature [27,31]. Anthocyanin content was affected by thermovinification when the treatment was very prolonged, or above 70 °C.

Concerning the effect of pre-fermentation heating on aroma, it has been reported that wines have a standardized sensory profile often described by oenologists as “banana yogurt” [32]. For example, varietal aromatic compounds with green pepper aromas (methoxypyrazines) decreased in Cabernet Sauvignon wines when they were thermo-treated [33]. Geffroy et al. [31] reported that a heat treatment at 70 °C for two hours induced a significant loss of several grape-derived aroma compounds (terpenols, norisoprenoids and some phenols) associated with an increase in α -terpineol, guaiacol and 2,6-dimethoxyphenol, suggesting thermal degradation. When thermovinification was applied to Carignan wine at two different temperature levels, 50 °C and 75 °C, and within two different time intervals, 30 min and 3 h, the effect of temperature on aroma composition was greater than that of heating time. Wines obtained from grapes treated at 50 °C had higher concentrations of geraniol, β -citronellol, β -damascenone, and 3-mercaptohexanol, in most cases [27].

Although thermovinification reinforces anthocyanin extraction, the wines thereby obtained are known to lack color stability and structure. Anthocyanins can decrease due to enzymatic hydrolysis [34], to combination with proteins, or to re-fixation with solid parts such as the skin [35] and yeasts [36]. Since no alcohol is present at the time of heating, the wine does not contain sufficient levels of tannin to stabilize unstable anthocyanins and to provide structure. As a consequence, wines obtained by thermovinification are not usually used for aging, but commercialized as table wine for everyday use.

Finally, since tannin extraction is much more dependent on increasing ethanol content to encourage its solubilization, one approach to obtain a higher extraction of polyphenolic compounds consists in fermenting grapes after heating with solid parts of the grapes, as in standard vinification with shorter maceration time. This alternative was found to increase total phenolic index, color intensity and anthocyanins content in wine 58%, 25% and 45%, respectively [29].

2.2. Flash Release

2.2.1. Description of the Technique

The process called “flash release” or “flash détente” consists in rapidly heating the grapes at temperatures between 85–95 °C by a direct injection of steam. Grapes are then introduced into a vacuum that instantly vaporizes the water, thereby cooling the treated grapes and weakening their skin cell envelopes by boiling the water inside the cells [37]. This effect on the skin cells enhances

extractability in subsequent fermentation process that may be conducted with or without the solid parts of the grapes. A modification of this process is called “half” flash détente [38]. It uses a weaker vacuum to cool the grape mash to around 50 °C instead of 30 °C.

2.2.2. Equipment

Flash release or flash expansion equipment consists of a heat exchanger and a vacuum chamber. In the heat exchanger, the steam is directly injected to the grape mash. Grape mash is continuously moved by two hollow stem augers through which the steam enters into the vacuum chamber. Since the chamber is under negative pressure (20–25 hPa), the water instantly evaporates, while the grape mash is simultaneously cooled. The estimated amount of evaporated water ranges between 6 to 10% [39]. It is condensed in a condenser connected with the vacuum chamber, and reincorporated into the grape mash totally or partially, depending on the amount of water in a gaseous state added to the grape mash during the heating process. The flash release system requires a boiler to produce water vapor for rapid heating.

2.2.3. Impact of the Treatment in the Composition of Wine

It has been reported that the yeast population lag phase before starting fermentation is slightly shorter when the grape mash is treated by flash release, probably because the treatment has triggered the release of some yeast nutrients [40].

Characteristics of wines obtained by flash release can be modulated by conducting fermentation in liquid phase, or by keeping the solid parts of the grapes in contact with the liquid phase for different periods of time. It has been observed that flash release increases the extraction of flavanols and flavonols from skins rather than from seeds. Therefore, when fermentation is carried out without the skins, the concentration of tannins with respect to anthocyanins is low, as in wines obtained via traditional pre-fermentation heating. The destabilization of grape skin cell envelopes seems to facilitate the extraction of tannins located in the vacuoles of the hypodermal cells of the grape skins. However, the proportion of those tannins in the resulting wine is low compared with the tannins coming from the seeds, which require the presence of ethanol to be extracted and also a more maceration time [41].

Morel-Salmi et al. [13] investigated the phenolic extraction kinetics during the maceration-fermentation of Grenache must previously treated by flash release. They observed that the amount of various families of phenolic compounds was higher at the beginning of the fermentation process in the flash release treated must than in control. On the other hand, while the levels of catechins, flavonols, and proanthocyanidins increased during fermentation of flash release treated musts, the concentration of hydroxycinnamic acids remained constant and anthocyanins decreased during the first day, and then they remained constant. The increment in concentration of galloylated units increased throughout fermentation, reflecting the gradual extraction of seed tannins as the ethanol level increased. Therefore, although the effect of flash-release on grape skin cell envelopes is more drastic than that of other pre-fermentation heating techniques, a contact period of the solid parts of the grapes with the must during fermentation after treatment is required in order to obtain structured wines with large amounts of polyphenols. At the of the vinification process, the wine obtained with Grenache grapes treated by flash release had a total phenolic index and a colour intensity 14% and 9% higher than the control wine respectively.

The effect of flash release on the extraction of aromatic compounds and aroma precursors has been also investigated [42]. As compared to wines obtained by other pre-fermentation heating techniques, wines obtained with flash release maintain their varietal aromatic profile. The treatment increases the levels of fatty acid ethyl esters and β -ionone in Grenache wines. On the other hand, it has been observed that flash release may reduce the content of C6 compounds responsible for herbaceous aromas [43]. This effect is especially interesting when the wines are elaborated with grapes that have not reached their optimal stage of maturity.

Wines of different varieties such as Grenache, Carignan, Syrah, and Mourvedre obtained with flash expansion technique were preferred to control wines in a sensory analysis, especially when the contact time of the solid parts of the grapes with the fermenting must was extended [44].

3. Non-Thermal Techniques for Improving Polyphenol Extraction

Non-thermal technologies have been one of the most frequently investigated topics in the field of food processing over the last decades [45]. The “non-thermal” concept refers to a group of technologies whose effects in foods are similar to those caused by heating, albeit at temperatures lower than the ones used in thermal processing. Some of these treatments may involve heat due to the generation of internal energy (e.g., resistive heating during PEF). However, they are classified as non-thermal, because they can eliminate or significantly reduce the application of high temperatures in food processing, thereby avoiding the deleterious effects of heat on the flavor, color, and nutritive value of foods.

The emergence of non-thermal technologies can lead to high quality products while saving energy by improving heating efficiency. Most of these technologies are locally clean processes and therefore appear to be more environment-friendly, with less environmental impact than traditional ones [46]. Novel processing technologies are increasingly attracting the attention of food processors, since they can provide food products with improved quality and a reduced environmental footprint, while reducing processing costs and improving the products’ added value.

Due to their special mechanism of action, pulsed electric fields and high-intensity ultrasound are among the non-thermal technologies that have been most investigated with the purpose of improving polyphenol extraction in wineries.

3.1. Pulsed Electric Fields (PEF)

3.1.1. Description of the Technique

PEF processing consists in the intermittent application of short duration pulses (ms- μ s) of high voltage (kV) to a product located between two electrodes. The applied external voltage generates an electric field whose strength depends not only on voltage intensity, but also on the distance between the electrodes. When exposed to a sufficiently strong electric field, the cell membrane undergoes a phenomenon called electroporation, consisting in the increment of cell envelope permeability as a consequence of the formation of pores in the cytoplasmic membrane [47].

If the intensity of the electric field is not high enough, or if the exposure to the electric field is sufficiently brief, the membrane can spontaneously return to its initial state and remains viable (reversible electroporation). However, intense electric fields or longer exposures can cause irreversible electroporation [48]. Reversible electroporation is a procedure that is typically used in molecular biology and in clinical biotechnological applications to gain access to the cytoplasm for the introduction or delivery in vivo of drugs, oligonucleotides, antibodies, plasmids, etc. However, the main applications of PEF in the food industry aim to cause irreversible electroporation of the cell membranes. It has been demonstrated that irreversible modification of the permeability of cell membranes can inactivate vegetative cells of microorganisms, enhance mass transfer in different operations of the food industry (e.g., extraction of intracellular components of interest, dehydration, infusion of compounds into the cells, etc.), and modify food structure [49,50].

3.1.2. Equipment

Basic components of an apparatus for the application of PEF are a pulse generator and a treatment chamber. The pulse generator is a Marx generator of square waveform pulses with a direct current power supply which converts alternating current to direct current line that is used, in turn, to charge a set of capacitors at high voltage. When the high voltage switch (a high-power solid-state switch) is opened, the capacitors are charged. If the high-power switch is then closed, all the electrical energy stored in the capacitors is delivered to the treatment chamber. The switching system permits

the controlled discharge of the capacitor in the form of pulses of very short duration at very high frequencies (reaching hundreds of pulses per second).

During PEF processing, a liquid food or pumpable product is passed through a treatment chamber where it is subjected to short pulses of high voltage. The treatment chamber consists of two electrodes made of a conducting material such as stainless steel or titanium; they are separated by an insulating material, which forms an enclosure containing the food material. Different types of treatment chambers have been designed to minimize the effect of electrolysis as well as corrosion. The two most important treatment chamber designs that are presently considered for the commercial application of PEF are parallel electrode and co-linear configurations. The latter configuration is the one habitually used for processing crushed grapes after destemming, with the purpose of electroporating the cytoplasmic membrane of grape skin cells to facilitate the extraction of polyphenols during the maceration-fermentation stage. The co-linear treatment chamber consists of an electrically insulating tube through which the grape mash flows. The electrodes are located in the middle (high voltage) and on either side of the chamber (ground). They consist of two metal pipes that also serve as the entrance and exit for the fluid. The circular section of this co-linear configuration facilitates its installation in winery circulation pipes used to transport crushed and destemmed grapes to the fermentation-maceration tanks (Figure 1) [51].

The lack of reliable and viable industrial-scale equipment has limited the commercial exploitation of PEF in the food industry for many years. However, recent developments in pulse power generators have enabled the design of PEF equipment with characteristics that can meet industrial standards in terms of reliability and workloads [52].

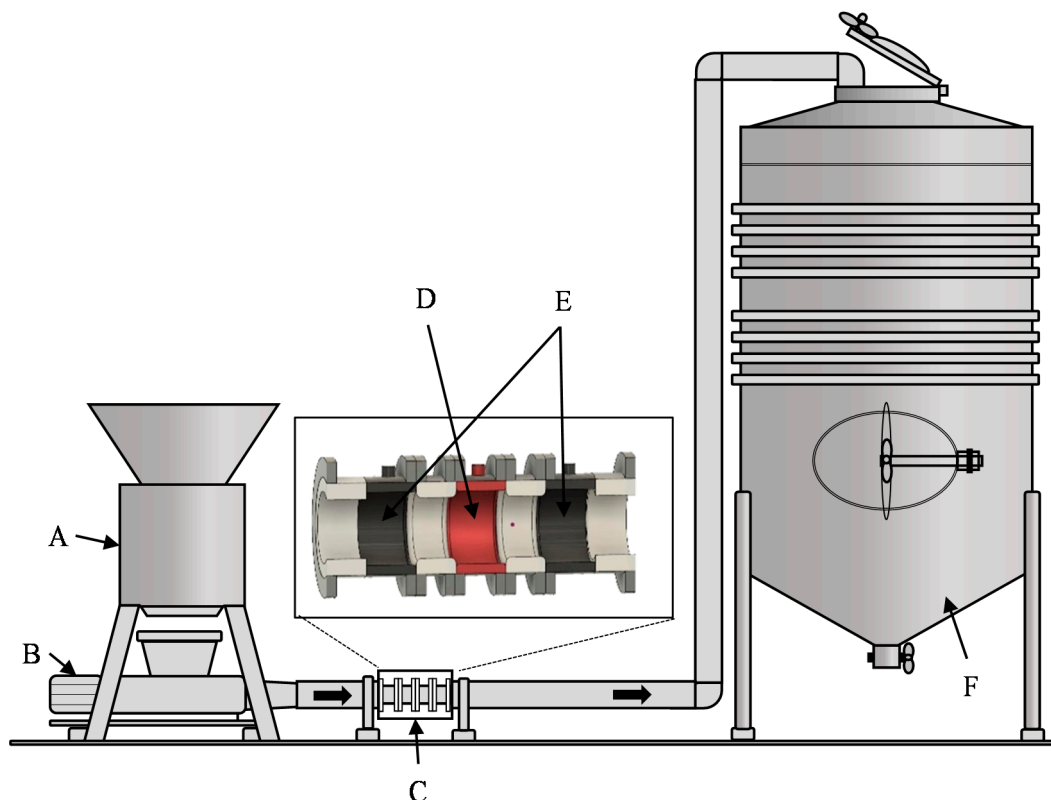


Figure 1. Flow chart of grape processing with PEF technology. (A) destemming; (B) progressive cavity pump; (C) co-linear treatment chamber; (D) high voltage electrode; (E) ground electrode; (F) fermentation tank.

3.1.3. Impact of the Treatment in the Composition of Wine

As compared with heating techniques, of the improvement of extraction of polyphenols by PEF requires to maintain the solid parts of the grapes in contact with the liquid phase for different periods of time [53]. Therefore, the effect of PEF treatment on cell skin envelopes seems to be less aggressive than that of techniques based on heating [54]. Tests carried out by different authors on different grape varieties agree that PEF treatment neither affects the fermentation process nor the physicochemical properties of the resulting red wine. Ethanol content, pH, volatile acidity and total acidity in the wines obtained with grapes treated by PEF were similar to control wines [53,55].

The electroporation of cell grape skins by the application of PEF accelerates and increases the extraction of phenolic compounds during the maceration-fermentation stage in the vinification of red grapes [56]. Different studies have shown that, after the same maceration time than in control wine, PEF treatment reinforces oenological parameters by a rate of 10% to 60%, depending on the extraction of polyphenols (color intensity, total anthocyanin content, and total polyphenol content) in the maceration-fermentation stage [53].

Puértolas et al. [57] showed that PEF technology can help reduce maceration times. Cabernet Sauvignon wine obtained from PEF-treated grapes (5 kV/cm, 150 μ s, and 3.67 kJ/kg) presented higher color intensity, total anthocyanin content, and total polyphenol content values, although the duration of the maceration of the grapes treated by PEF was 48 h shorter than for control wines. Evolution during aging of the wine obtained from grapes treated by PEF was similar to control wine. The differences in color intensity, total anthocyanin content, and total polyphenol content observed at the end of fermentation between control wine and the wine obtained from PEF-treated grapes were maintained after aging the wine in bottle or oak barrels [58]. Determination of individual polyphenols by means of high-performance liquid chromatography (HPLC) highlighted that the wines obtained by PEF treatments did not show differences in terms of the proportion of different polyphenols, thus indicating that PEF treatment did not selectively extract phenolic compounds from grape skins. López-Alfaro et al. [59] reported that the content of resveratrol, one of the most researched phenols in wine due to its beneficial properties, increased by a proportion of 200, 60 and 50% in Tempranillo, Garnacha and Graciano, respectively, when the grapes were treated with PEF before maceration-fermentation.

Energetic requirements for the electroporation of cells of grape skins are lower than 10 kJ/kg; as a consequence, the treatment causes an increment of less than 2 °C in grape mash temperature. This low impact allows the obtained wines to maintain their varietal character [57]. Some experiments have shown that PEF treatments encourage the diffusion of aromatic compounds found in the skin, as well as of aromatic precursors [60]. PEF treatment did not increase the concentration of C6 family compounds associated with herbaceous aromas in wines obtained from Garnacha, Tempranillo, and Graciano varieties [60]. The treatment significantly increased monoterpenoid compounds, and had a positive effect on the concentration of β -ionone, total esters, and benzenoid compounds in Grenache wine. However, the volatile composition of Tempranillo and Graciano wines was not affected by PEF.

Sensory analysis did not detect any drawbacks in Cabernet Sauvignon wines obtained with grapes treated by PEF. Luengo et al. [51] compared Grenache wines featuring similar enological parameters in terms of polyphenol content obtained, on the one hand, with PEF treated grapes and 7 days of maceration and, on the other hand, with untreated grapes and 14 days of maceration. Compared with control wine, panelists preferred the wine obtained with grapes treated by PEF and a shorter maceration period.

3.2. Ultrasound

3.2.1. Description of the Technique

Acoustic waves of a specific frequency lying above the detection threshold of human hearing (i.e., over 16–18 kHz) are designated as ultrasound. Ultrasound is divided into two categories, according to the frequency range and the intensity of ultrasonic waves. The first group, commonly known

as high-intensity ultrasound, features low frequency and high intensity (20–100 kHz; $>10 \text{ W/cm}^2$). The second group, commonly called diagnostic ultrasound, uses high frequency and low power ($>100 \text{ kHz}$; $<1 \text{ W/cm}^2$).

When high-intensity ultrasound passes through a liquid medium, a phenomenon called acoustic cavitation occurs [61]. Cavitation consists in the implosion of bubbles formed in liquid media when the local pressure in the expansion phase falls below vapor pressure. During the implosion, it is estimated that high temperatures and pressures are reached in very small spots and very short periods of time: liquid jets of up to 280 m/s are likewise generated. These phenomena brought about by cavitation are responsible for effects attributed to high-intensity ultrasound, such as the increment of mass transfer, or the breakage of cells of microorganisms, or of plant or animal tissues [62]. Ultrasound may therefore enhance the extraction of polyphenols from the solid parts of grapes in red winemaking by breaking up the cells, and by facilitating the diffusion of polyphenols from the cells to the must [63].

3.2.2. Equipment

An apparatus for the generation of ultrasound consists in a power supply and a transducer. The power supply converts alternating current line voltage to frequencies of over 20 kHz electrical energy. This high-frequency electrical energy is fed to a transducer, where it is converted to mechanical vibrations at the same frequency as the transformed electrical current. The physical concept underlying the transducer is the piezoelectric effect: the property of certain materials causes them to change shape when an electric current is applied to them. An ultrasound transducer contains a thin disk, square, or rectangle of piezoelectric ceramic placed between two electrodes which expand and contract when subjected to alternating voltage. The converter vibrates in a longitudinal direction and transmits the motion to the solution, thereby causing cavitation [61].

A power ultrasound system has recently been developed for processing destemmed and crushed grapes in continuous flow. The equipment consists of a hexagonal stainless-steel pipe into which the transducer is welded (Figure 2). The length of the pipes containing the transducers is variable, depending on the installation's processing capacity, which can reach up to ten tons per hour. The cavitation caused by the ultrasound treatment provokes the destruction of the cells of the solid parts of the grapes, thereby leading to the release of polyphenols.

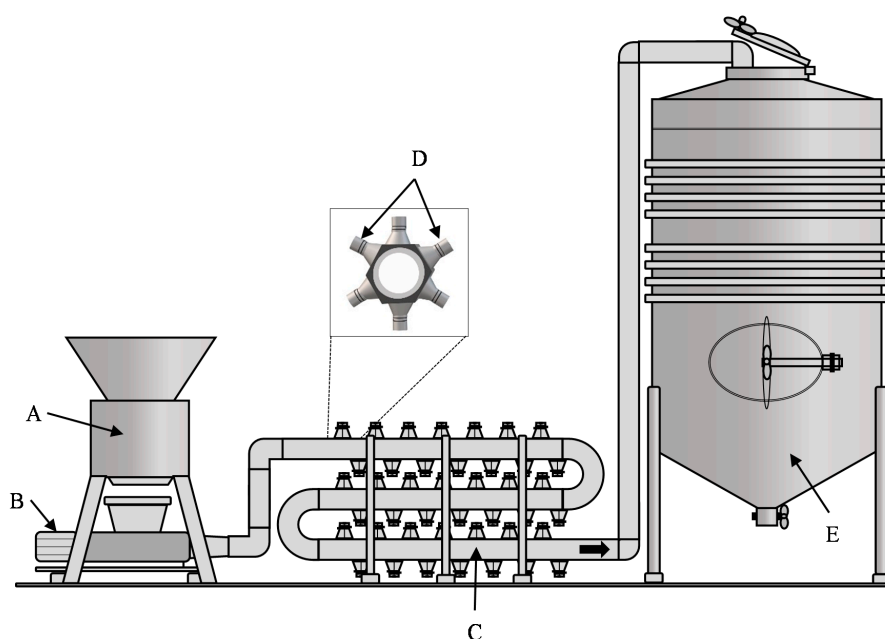


Figure 2. Flow chart of grape processing with ultrasound technology. (A) destemming; (B) progressive cavity pump; (C) ultrasound treatment zone; (D) transducer; (E) fermentation tank.

3.2.3. Impact of the Treatment in the Composition of Wine

The use of high-power ultrasound (US) to improve the extraction of phenolic compounds from grapes has been recently studied [64,65]. As in the case of PEF technology, an ultrasonic treatment applied at different frequencies (45, 80, and 100 kHz) with the purpose of improving polyphenolic extraction did not modify the physicochemical properties of wine. Total acidity and pH of Cabernet Sauvignon wine obtained from ultrasound-treated grapes did not show significant differences with respect to control, although electrical conductivity was slightly higher (4%). This increment in conductivity could be associated with the release of ions located inside the cells of the solid parts of the grapes to the must [65].

El Darra et al. [17] investigated the effect of ultrasound on the extraction of polyphenols from Cabernet Sauvignon grapes at laboratory scale using an US probe in a flask containing 400 ± 5 g of must and grape skins. Results showed an increment in the phenolic, anthocyanin, and tannin contents of the wines obtained from grapes treated by ultrasound. A greater color intensity compared with the untreated samples was likewise observed in the wines after ultrasonication treatment, whereby the highest values of those parameters were achieved by the samples that had been subjected to the most intense treatment (363 kJ/kg).

Monastrell wines obtained after different maceration times with grapes treated by a continuous flow pilot-scale power ultrasound system (2500 W, 28 kHz, 8 W/cm²) were compared with wines obtained from untreated grapes [66]. Results showed an increase in the chromatic characteristics of the wines obtained with ultrasonicated grapes. The values for these chromatic characteristics were higher in wines obtained with ultrasonicated grapes and 3 days of maceration than in control wines with a longer maceration period (5 days). After two months of aging, the wines obtained with grapes treated by US contained between 20 and 35% more total polyphenols than control wines [66]. The ultrasound treatment also encouraged the extraction of tannins from the seeds, although to a lesser extent than tannins from the skins. As a consequence, the wines elaborated with ultrasonicated grapes and 3 days of maceration presented twice the concentration of proanthocyanidins than that of control wines obtained with 8 days of maceration.

Concerning the effect of ultrasonication treatment on the volatile composition of wines, no significant differences were observed in the total concentration of those compounds between control and wine obtained from grapes treated by ultrasound, regardless of maceration time [63].

4. Discussion

Novel non-thermal processing technologies have been developed in the last years with the aim of preventing problems associated with thermal processing, and with the purpose of improving energy efficiency and food production sustainability. The introduction of a new technology on the market requires that it must perform at least as well as existing commercial processes. Table 1 compares, as an example, the improvements derived of application of different thermal and non-thermal physical methods to the grapes before vinification in terms of polyphenolic extraction. It is observed that PEF and ultrasound permits attaining similar enhancements in total anthocyanin content, color intensity and total polyphenol content than techniques based in the heating of the grapes. However, as it is shown in Table 2 thermovinification and flash release present certain drawback related with the wine quality, energy consumption etc. that would support the implementation of non-thermal physical techniques to improve polyphenol extraction.

Although in the past decades the food industry has carried out immense efforts to optimize energy consumption and heat recovery in conventional processes, the introduction of non-thermal technologies may yet provide a further potential to help reduce energy consumption and operational costs while improving food production sustainability. Table 3 compares the energy delivered to grapes (after destemming and crushing) by several thermal (with final treatment temperatures between 50 to 85 °C before fermentation) and non-thermal processes (with temperature increases lying under 5 °C) to obtain an equivalent effect in terms of polyphenol extraction in red winemaking. One can

observe that the energy required to increase the temperature of grapes is much higher than the energy required to electroporate grape skin cells by PEF, or to disrupt skin and seed cells by ultrasound. From an energetic point of view, non-thermal techniques present an additional advantage, since the low energy delivered to the product does not substantially increase its temperature. As compared with thermovinification or flash release in the case of winemaking, this implies that it is not necessary to waste energy to cool the grape mash to the temperature required to initiate fermentation. According to Table 3, the average specific energy of thermal treatments is 17.6-fold higher than that required for non-thermal processes being the specific energy required for PEF treatment lies 3.2-fold lower than that required by ultrasound treatment. Consequently, considering that the energy source is different for thermal and non-thermal processes, lower operational costs are required for PEF and ultrasound processing. From an energetic point of view, another important issue when comparing thermal and non-thermal technologies is that, in the latter processes, energy is delivered directly to the product, thus making such methods much more efficient than heating techniques where thermal energy is transferred through an intermediate medium (water, water vapor, or oil). While thermal techniques require water, non-thermal techniques permit to obtain similar objectives without increasing water consumption in a winery. As a consequence, non-thermal technologies are considerably more sustainable: they reduce the use of resources as well as CO₂ emissions.

Another aspect that differentiates thermal from non-thermal techniques is related with the installation of the unit in the winery. The required space for the installation of thermovinification or flash expansion is much greater than that required for the installation of ultrasound or PEF units. Generally, considerable renovation is required for a winery to introduce a thermovinification or a flash expansion unit with associated auxiliary units. PEF technology differs from other techniques in view of its portability. The pulse generator unit is separate from the treatment chamber, thereby allowing a rapid adaptation of the process, depending on the product to be treated. Moreover, these units are small enough to be easily integrated into existing production lines without requiring major factory overhaul.

To summarize, non-thermal techniques such as PEF and ultrasound are now increasingly attracting the attention of wineries as an alternative to techniques based on grape heating in order to reduce the duration of maceration time and/or to avoid the purchase of maceration-fermentation tanks. These techniques can encourage the production of wine with improved quality and a reduced environmental footprint, while at the same time decreasing processing costs.

Table 1. Improvements derived of grape treatment before vinification with different thermal and non-thermal physical methods in terms of increment in total polyphenolic content, color intensity and total anthocyanin content.

Technology	Treatment	Variety	Total Polyphenolic Content	Colour Intensity	Total Anthocyanin Content	Ref.
Thermovinification	82 °C 1 h Flow rate: 500 kg/h Maceration time: 5 days	Merlot	36%	N/A	26%	[28]
Flash-release	95 °C for 6 min Strong vacuum (>100 mbar) Flow rate: N/A Maceration time: 5 days	Carignan	11%	30%	30%	[13]
PEF	5 kV/cm, 150 µs (50 pulses 3 µs, 3.67 kJ/kg) Flow rate: 118 kg/h Maceration time: 4 days	Cabernet Sauvignon	23%	38%	34%	[57]
Ultrasound	2500 W; 28 kHz; 8 W/cm ² Flow rate: 400 kg/h Maceration time: 4 days	Monastrell	32%	31%	13%	[66]

N/A: information not available.

Table 2. Advantages and disadvantages of different thermal and non-thermal technologies for improving polyphenol extraction in red winemaking for grape pre-fermentation treatments.

Technology	Advantage	Disadvantages	Ref.
Thermovinification	Possibility of obtaining red wines without maceration For obtaining table wines. Permits to inactivate enzymes and microorganisms Approved by OIV	Poor color stability Possible degradation of anthocyanins Loss of varietal aromatic compounds Wines not usually used for aging Addition of starter cultures for initiating fermentation required High energetic requirement. Supplies of methane or diesel oil required	[12,25,27–29]
Flash-release	Mainly for obtaining table wines. Permits to inactivate enzymes and microorganisms Obtaining of more complex sensory characteristics Approved by OIV	Possible degradation of anthocyanins Wines not usually used for aging Addition of starter cultures for initiating fermentation required High energetic requirement. Supplies of methane or diesel oil required Renovations are required in the winery for installation (Large facilities: >100 m ²)	[13,39,44]
PEF	Demonstrated the ability of aging of the wines in oak barrels Easy implementation in the winery (small facilities:<10 m ²) Possibility of renting the PEF unit Possibility of conducting fermentations with wild yeast Possibility of using for other applications in winery (microbial inactivation or accelerating aging on the lees) Low energy requirements	Maceration of few days is required for obtaining red wines Approval for the OIV in process. No enzymatic inactivation.	[16,51,53,58]
Ultrasound	Easy implementation in the winery (small facilities:<10 m ²) Possibility of renting the ultrasound unit Possibility of conducting fermentations with wild yeast Possibility of using for other applications in winery (accelerating aging on the lees) Low energy requirements	Maceration of few days is required for obtaining red wines Approval for the OIV in process. No enzymatic inactivation.	[66–68]

Table 3. Estimation of the energetic costs of thermal and non-thermal physical methods for improving polyphenol extraction during winemaking.

Technology	Specific Energy Delivered to the Grape (kJ/kg)	Additional Specific Energy * (kJ/kg)	Total Specific Energy (kJ/kg)	kWh/tn	€/tn ^a
Thermovinification	161.92	40.68	202.6	56.28	7.32
Flash-release	251.88	45.86	297.7	82.70	10.75
PEF	6.70	-	6.70	1.86	0.24
Ultrasound	21.60	-	21.60	6.0	0.78

^a Energy cost: Electricity: 0.13€/ kWh, * The energy required for the complete operation of the thermal system (pumps, refrigeration and condensation systems).

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