High-Voltage Electrical Discharge-Assisted Extraction of Phenolic Compounds from Grape Seeds

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Abstract

This chapter will discuss the high voltage electrical discharges assisted extraction of phenolic compounds from grape seeds. The grape seed, its morphology, and chemical composition are discussed in the first section. In the second section the conventional extraction processes (solid liquid/extraction) and pulsed electric field assisted extraction are compared and discussed. Finally, a special section

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will be dedicated to high voltage electrical discharge (HVED) in liquid–solid mixture as an extraction process, as it has shown interesting results on this particular raw matter. In this chapter, HVED refers to the formation of an electric arc in a liquid short-circuiting two electrodes, and inducing number of physical phenomena. It is a process that combines the effects of pulse electric field (PEF) with the fragmentation of the raw material. However, HVED is very different from PEF. The physical phenomena related to HVED in water are also complex and not perfectly controlled and understood. The last subsection will adress these phenomena and their relation with the extraction process. The basic knowledge related to HVED (the underlying physics and the material used) will be summed up in order to help understanding this extraction method.

Keywords

Grape seeds • Polyphenols • Extraction • High voltage electrical discharges • Pulsed electric field

Contents

Introduction

Grape seeds are known to be an especially rich source of polyphenols. As such, many investigations on polyphenol extraction from grape seeds have been led over the past decades. Polyphenols compose a family of biologically active molecules sought by pharmaceutical and cosmetic industry for their antioxidant and antiaging properties. Conventional polyphenols extraction from grape seeds is usually a simple solid–liquid extraction performed through the use of organic solvents. New nonconventional technologies, and especially electrotechnologies, have been tested in order to enhance extraction rates and possibly reduce the use of solvents. High voltage electrical discharge (HVED) has shown interesting results on this particular raw matter.

This chapter is divided in three subsections:

1. The grape seeds, its morphology and biochemical composition. In this subsection, phenolic compounds and their biological activities, and the most usual methods for polyphenols dosing will be also discussed.
2. Conventional extraction and a brief summary of the influence of different parameters on the extraction. The use of pulsed electric field will also be considered in this subsection.
3. High voltage electrical discharges as a mean of extraction and its use on grape seeds.

In this chapter, the emphasis is put on the last subsection. The basic knowledge on HVED, which is necessary to conduct studies using this process, will be briefly explained. These basics are composed of the physical phenomena induced by electric arcs in liquids and leading to the extraction, of some insights on the materials used to achieve HVED, and finally of the underlying physics of the electric discharge's inception and propagation.

Grape Seeds

Grape Production

Grape (*Vitis Vinifera* L.) is one of the most widespread fruit crops with a production reaching 77 million tons in 2013 according to the Food and Agriculture Organization (FAO) statistical database (2013). World grape production has undergone a significant rise over the past few years mostly through the expansion of winemaking industry in China, which is now the world's largest grape producer.

Roughly 80% of grapes are used for wine production while the remaining 20% are eaten as table grape. Grapes used for wine production are pressed, generating wastes called grape pomace composed of 3% stems, 70–80% skins and 10–20% grape seeds. Grape pomace contains an exceptionally high amount of phenolic compounds, natural antioxidants presenting a wide range of positive biological activity. Hence, this by-product of wine industry is used as an abundant and low cost source of natural antioxidants by cosmetic and pharmaceutical industries, and extraction of phenolic compounds from grape seeds has become an important issue and has been investigated through numerous studies.

Grape Seed Morphology

A typical grape seed structure is presented in Fig. 1. It consists of an embryo surrounded by the endosperm (or albumen), which is covered by a three-layer integument forming the hard shell of the seed. Finally, a thin cuticle (the epidermis) covers the shell.

The endosperm, which purpose is to provide nutrition to the embryo, is rich in proteins and lipids. The lipids contained in the endosperm are mainly presented by

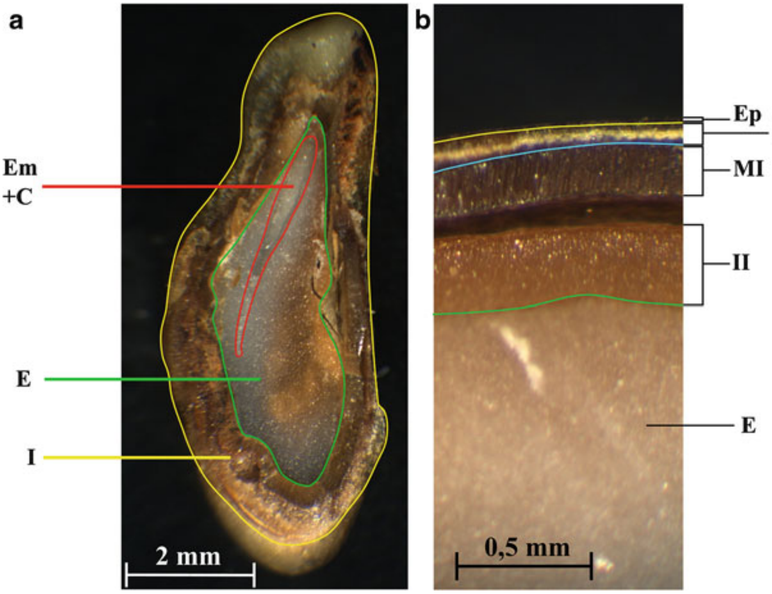


Fig. 1 (**a**) Sectional view of a grape seed. *Em* embryo, *C* cotyledon, *E* endosperm (albumen), *I* integument. (**b**) Close-up on the integument region of the grape seed. *Ep* epidermis, *OI* outer integument, *MI* middle integument, *II* inner integument

linoleic (60–75%) and oleic (13–24%) acids (Lutterodt et al. 2011), and they are sought for the production of grape seed oil.

The integument's purpose is to provide mechanical and chemical protection to the embryo and the endosperm. The mechanical protection is assured by the presence of lignin in the middle integument (Cadot et al. 2006). Lignin is a structural phenolic polymer that typically makes up 15–30% of usual wood (angiosperm and gymnosperm). Because of its hydrophobicity, lignin accumulates on cellular walls and thus confers rigidity to the cells and to the overall structure. The lignin inside the middle integument has also the role of protecting the endosperm from oxidation and confers impermeability to the seed. Other phenolic compounds like tannins and flavan-3-ols are mainly located in the inner and outer integument. The role of these phenolic compounds is to protect the seed against mushrooms and insects and to prevent gaseous exchanges with the external environment (Cadot et al. 2006). However, being secondary metabolites, the polyphenols location, repartition, and quantity differ greatly according to the grape variety and the harvest conditions (place, year, maturation time) (Xu et al. 2009).

Biochemical Composition of Grape Seeds

The overall biochemical composition of ripe grape seeds (coming from ripe grapes before pressing) is given in Table 1. The grape seed growth has an effect on the size and the biochemical composition of the grape berry. The weight, the sugar content, and the acid composition are related to the number of grape seeds in the berry (Ribereau-Gayon 1968). Apart from polysaccharides that can be found in each part of the seed, the other biochemical compounds have specific locations. For instance, proteins and lipids can only be found in the endosperm.

Phenolic Compounds in Grape Seeds

Phenolic compounds are secondary metabolites found in every plant. Their qualitative and quantitative repartition changes significantly according to the plant variety, the specific organ considered, and the maturity stage. Thus, it is difficult to compare two different kinds of grape seed, as the quantity and nature of their phenolic compound change according to the harvest year, the crop location, and the grape variety. It has been reported that, according to the grape variety, phenolic compounds constitute roughly 1–10% of the total dry seed mass (Xu et al. 2009).

The main interest of phenolic compounds is their antioxidant activity, which takes place through several mechanisms. The first mechanism is the inhibition of the activity of oxidizing enzymes like oxidoreductase or lipoxygenase. The second mechanism is free radicals scavenging. Free radicals are responsible of destructive chemical chain reactions that are thought to be responsible of aging. Free radicals capture is illustrated in Fig. 2 (Choe and Min 2006). Finally, some polyphenols are able to chelate metallic ions, which are catalyst for oxidizing reactions.

These properties lead to medical applications like skin cancer therapy, inhibition of the oxidation of human lipoproteins, anti-inflammatory effects, etc.

The different kinds of phenolic compounds that can be found in grape seeds are described below and are illustrated in Fig. 3 (Guendez et al. 2005).

Table 1 Chemical composition of a grape seed in % of fresh weight

Water	25–45
Carbohydrates	34–36
Lipids	13–20
Tannins	4–10
Nitrogen compounds	4–6.5
Minerals	2–4

Adapted from Flanzy (1998)

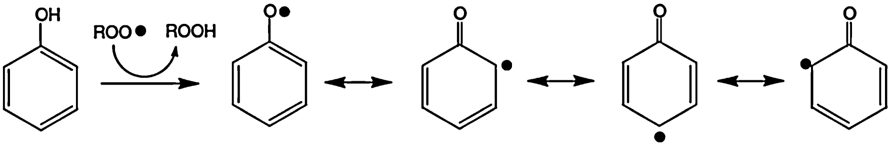


Fig. 2 Capture and stabilization of a radical via resonance (Retrieved from Choe and Min (2006) with permission)

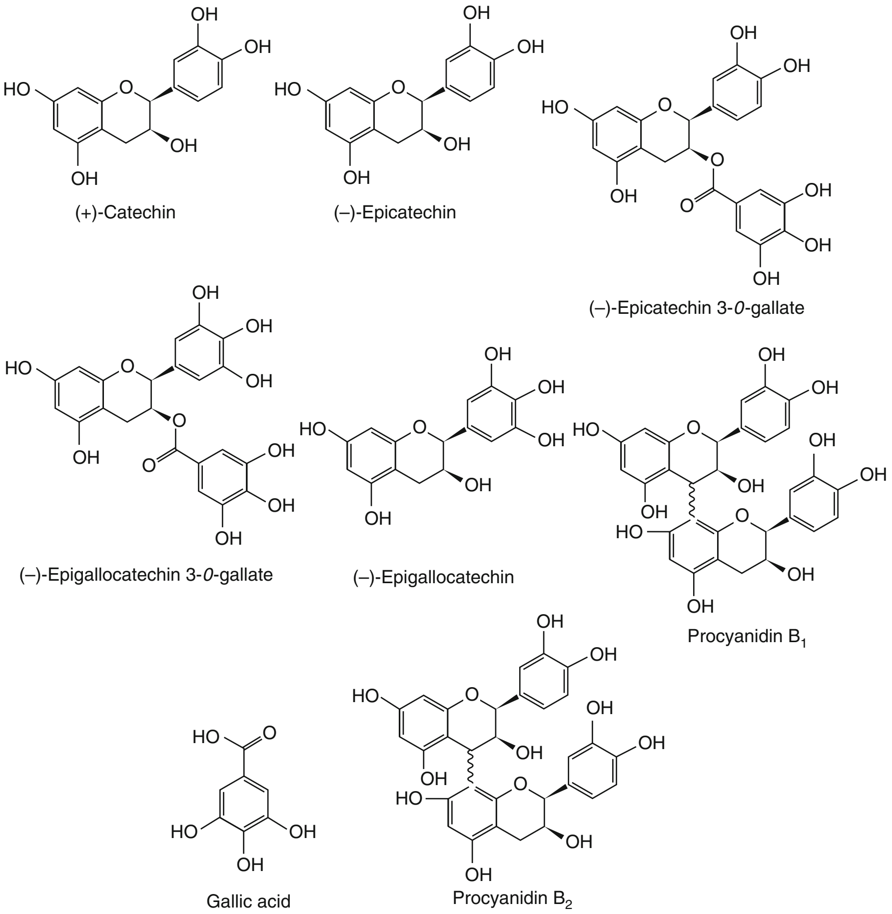


Fig. 3 Name and chemical structure of typical phenolic compounds found in a grape seed (Retrieved from Guendez et al. (2005) with permission)

Phenolic Acids

Phenolic acids are the simplest forms of phenolic compounds. They can be separated into two categories: those derived from hydroxybenzoic acids and from hydroxycinnamic acids.

Hydroxybenzoic acids are phenolic monomers derived from benzoic acid, with a carbon structure in C6–C1. Hydroxycinnamic acids are derived from cinnamic acid with a carbon structure in C6–C3. Hydroxycinnamic acids are rarely observed as simple monomers in nature and are more frequently present as glycosides or esters (with tartaric acids, quinic acids, or glucose). The more abundant phenolic acids in grape seeds are Gallic acids (a hydroxybenzoic acid) and p-comaric acid (a hydroxycinnamic acid).

Stilbenes are another class of derivatives of hydroxycinnamic acid, with a basic structure of two benzene rings linked by an ethylene bridge. Stilbenes can be present in grape seeds as trans-resveratrol, but these molecules are generated by the plant only when exposed to stress, for instance, parasitic diseases.

Flavonoids

Flavonoids have a general structure in C15 (C6–C3–C6). This class of metabolites includes thousands of different molecules and is classified in tens of subcategories. In each of these subcategories, there are a large variety of molecules, which differ on the level of hydroxylation of the different benzene rings, the level of methoxylation (replacement of phenol groups with $O–CH_3$ groups), and the level of glycosylation (connection of carbohydrates to the basic flavonoid structure). The flavonoids that can be found in grape seeds are mostly catechin, epicatechin, gallocatechin, and epigallocatechin, which are all flavan-3-ols, a flavonoid subcategory. Quercetin and other polyphenols from the subcategory of flavonoid called flavanols can also be found in smaller quantities.

Condensed Polyphenols

Condensed polyphenols are dimers or polymers of simpler phenolic compounds like flavonoids. Procyanidin B1 and B2 can be abundantly found in grape seeds. These molecules are polymers of flavan-3-ols, and are often referred as condensed tannins. In grape seeds, procyanidins are usually found in dimeric or trimeric forms, but rarely at a higher polymerization degree.

Lignin is another kind of condensed polyphenol commonly found in grape seeds. Lignin basically forms from the three-dimensional polymerization of three different phenolic units derived from hydroxycinnamic acid: p-coumaric, ferulic, and synapil acids. Lignins are heavily polymerized molecules, and their purpose is mainly to confer rigidity to the seed's structure.

Common Phenolic Compound Analysis

The most usual kind of analysis to determine the total polyphenol content of a sample is the Folin-Ciocalteu method. It is a colorimetric method based on the oxidation of phenolic compounds and the reduction of the Folin-Ciocalteu reagent, composed of phosphotungstic and phosphomolybdic acids, which would produce a blue coloration. This coloration can be quantified on a spectrophotometer for a light wavelength of 750 nm. It has to be noted that the Folin reagent reacts to any reducing agent and not only to phenolic compounds. A simple and commonly used method has been proposed by Ribereau-Gayon (1968): 0.2 mL of the sample is mixed with 1 mL of a 1:10 diluted Folin-Ciocalteu reagent and after agitation, 0.8 mL of a 75 g/L solution of Na_2CO_3 is added. After another agitation, the mixture is either incubated for 10 min in a water bath at 60 °C or for 1 h at room temperature. The mixture takes a blue coloration that can be measured at 750 nm. For the quantification of polyphenol, gallic acid is often used as a standard to obtain a calibration curve. This way, the results are given in gram of gallic acid equivalent (GAE).

An easier method is based on the characteristic absorption of the benzene cycle around 280 nm (Mataix and Luque de Castro 2001). As all phenolic compounds are composed of benzene cycles, this method allows the quantification of phenolic compounds by directly measuring the absorbance of the sample in a spectrophotometer at 280 nm. This method has often shown good accordance with the Folin-Ciocalteu method and has the advantage of being much simpler.

The diverse phenolic compounds can be screened using high performance liquid chromatography (HPLC). This technique, described in Elena D. Katz (1995), allows the characterization and quantification of phenolic compounds.

Conventional and Pulsed Electric Field Enhanced Extraction

Conventional Extraction

Extraction of phenolic compounds from grape seeds is usually performed via a liquid–solid extraction, in which the principle is to put the solid raw matter in contact with a solvent. The solvent, very often a mixture of water and organic solvents (ethanol, acetone, methanol, ethyl acetate, etc.), will dissolve solutes formerly attached to the solid phase. After the extraction stage, the solvent containing the solutes is separated from the solid phase, purified from unwanted solutes, and then concentrated under the vacuum. The obtained concentrated extract is finally atomized and a powder of the wanted molecule is obtained.

The liquid/solid extraction has been extensively studied in order to maximize the yields.

Basically, three aspects govern the extraction yields:

1. The solubilization of the solutes, which depend on the solute-solvent affinity and the exchange surface extent.
2. The diffusion rate inside the solid and the liquid phase.
3. The solute concentration gradient in the boundary layer between solid–liquid phases.

Though, it is very difficult to compare two different studies on grape seeds polyphenol extraction, as the phenolic content greatly differs from one kind of sample to another.

However, tendencies have been observed over some important parameters.

Nature of the Solvent

Organic solvents are often used for phenolic compound extraction. Organic solvents present the advantage of interacting with biological membrane, which results in a reduction of membranes integrity (Sikkema et al. 1995). Thus, using these solvents increases the effective diffusion coefficient inside grape seeds. Also, according to the solvent used, the extraction can be more or less selective. The objectives of extraction are both to obtain the maximum yield of target solute and to get the purest

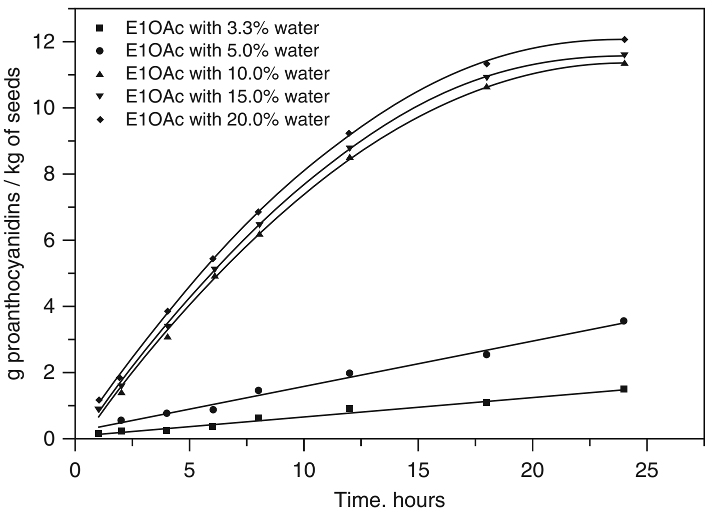


Fig. 4 Dependence of the yield of proanthocyanidins on extraction time and water content in ethyl acetate (Retrieved from Pekić et al. (1998) with permission)

extract at the end of the process in the cheapest way. However, extraction usually leads to extract a lot more molecules than just the target solutes, and a purification phase is needed. A selective extraction simplifies the purification process and thus moderates the cost of the overall process.

It has been shown that the use of ethyl acetate can lead to a selective extraction of flavan-3ols and proanthocyanidins (flavan-3ols polymers) from grape (Pekić et al. 1998). However, grape seeds are impermeable to this specific solvent and addition of water to ethyl acetate has shown very good extraction yields, as water helps the solvent to impregnate into the seed, as shown in Fig. 4. It has been shown that an addition of more than 10% water in ethyl acetate results in the extraction of too much unwanted solutes. This example illustrates the compromise between selectivity and yield rates when the issue of selectivity is considered. Ethanol and methanol has been both studied as solvents for polyphenols. Ethanol is less selective toward phenolic compounds than methanol, and phenolic extraction rates are slightly better with methanol (Pinelo et al. 2005). Nevertheless, ethanol is usually preferred over methanol, especially for food application, as it is a dietary alcohol.

Other Parameters

Temperature has important effect on extraction. A higher temperature induces weaker cell membranes, higher diffusion coefficient in both solid and liquid phase and higher solubility of the different solutes. Still, there is a temperature limit beyond which the phenolic compounds will become unstable and finally degrade (Lafka et al. 2007). This temperature limit varies from studies to studies from 50 to 60 °C. Maximum yields can be obtained working at these temperatures.

Grinding or crushing the seeds has a very strong effect on extraction time. Grinded grape seeds offer much more exchange surface, which results in much shorter extraction times (Pastrana-Bonilla et al. 2003). Some studies have shown that even if the extraction time is very different, maximum phenolic yields are similar for grinded and intact seeds (Pekić et al. 1998). Furthermore, grinding seeds lead to the extraction of a lot of unwanted solutes (i.e., lipids and proteins from the endosperm).

Low pH can positively affect the extraction of polyphenols. Indeed, polyphenols are more stable in acidic medium. An acidic environment also improves the solubility of phenolic compounds, weakens cell membranes and walls, and ultimately enhances polyphenol diffusion throughout the seed. It has been found that optimum pH for polyphenol extraction lies between 1.5 and 2.1 (Chirinos et al. 2007).

Extraction time is more problematic, as different studies lead to different conclusions. Some authors chose short extraction times, from 10 to 30 min, while others used longer extraction times, from 1 to 24 h. This may be explained by the presence of several stages of diffusion with different diffusion rates. The first stage shows a fast extraction of a certain percentage of the grape seed's polyphenols, lasting from 10 to 30 min, and the second stage is a slow extraction of the remaining polyphenols lasting from 1 to 24 h.

Pulse Electric Field Enhanced Extraction

Pulsed electric field (PEF) is a nonconventional treatment that tends to be widely used. The main effect of PEF is to noninvasively enhance mass transfer through a mechanism called electroporation. Electroporation, as its name implies, refers to the formation of small holes or pores inside the cell membrane under the influence of an electric field. The mechanism of electroporation is illustrated in Fig. 5. The cell membranes can be seen as capacitors that will charge when an external electric field is applied. When the transmembrane potential is high enough, the membrane is compressed by the electric charges, perforated and loses its barrier function. This mechanism can be reversible or irreversible.

PEF treatment allows the release of intracellular components and enhances diffusion in solid media. Few studies have been specifically performed on grape seeds. (Corrales et al. 2008) have compared PEF treatment, ultrasonic (US) treatment, high hydrostatic pressure (HHP) treatment, and a control extraction. The solvent was 50% water and 50% ethanol in all cases. The study has revealed that all treatments have a positive impact on phenolic compounds extraction compared to the control extraction. It also showed that even though there were few differences in extraction for US, HHP, and PEF, the antioxidant activity was clearly higher for PEF treatment.

Boussetta et al. have also investigated the effect of PEF and ethanol addition to the solvent. It was shown that the diffusion time, when PEF treatment in water-ethanol

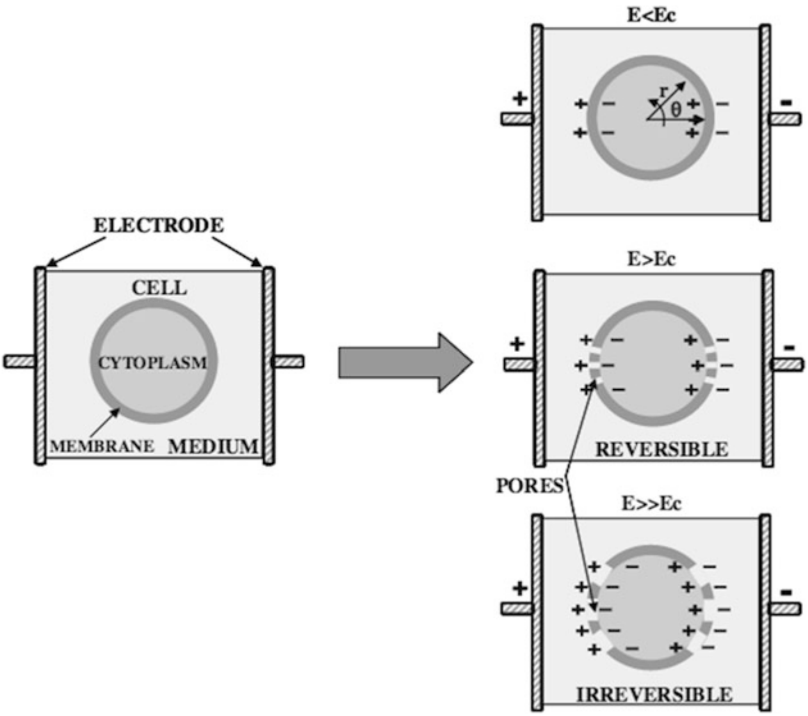


Fig. 5 Biological cell in an electric field E. Electroporated area is represented with *dashed lines*. *Ec* critical electric field strength (With permission from Donsi et al. (2010))

solvent was performed, is 3.7 ± 0.4 times shorter than the diffusion time of a simple liquid/solid extraction with the same solvent and in the same temperature condition.

Extraction with High Voltage Electric Discharges (HVED)

New methods of extraction have been investigated in order to reduce the environmental impact of conventional extraction methods. High voltage electric discharges (HVED) have shown very interesting results for the polyphenols extraction from grape seeds. Indeed, when applied in a liquid medium, HVED have physical features leading to the extraction of biomolecules from raw materials located inside the liquid medium. Though, the way this method allows extraction is quite different from pulsed electric fields. The main effect of HVED is fragmentation of raw materials. This fragmentation occurs through a certain number of physical phenomena, which will be discussed later. These physical phenomena are complex and the way they lead to extraction of raw material is not fully understood yet.

In this section, basics of HVED physics will be discussed. These basics are necessary to understand and manipulate HVED as an extraction technique.

The Electric Arc

An electric arc occurs when a high voltage is applied to a pair of electrodes in a dielectric media like air. If the electric field between the electrodes is high enough, a conductive plasma channel propagates from one electrode to the other. This phenomenon is often called streamer, or leader in some specific cases. It will be discussed later as it is a complex yet very important aspect of the formation of the electric arc. Plasma is an ionized gas partially made of ions and free electrons. Plasma is therefore conductive. When this plasma channel bridges the two electrodes, it acts like a resistor of very small value short-circuiting the two electrodes. Consequently, all the electrical energy available in the external circuit will be dissipated in this channel. This will lead to very large electric currents (kiloamperes) passing through this plasma channel. The consequence will be a very steep increase of the temperature due to Joule effect (thousands of degrees increase in nanoseconds). This extreme temperature change will have two observable effects that result to what is called an electric arc. The first visible effect is an intense light emission, with a peak in the V-UV ($\lambda = 100–200$ nm). The second effect is a steep increase in the plasma channel's pressure. This pressure increase, which goes simultaneously with the temperature increase, provokes an acoustic wave in the surrounding medium. Those light emission and acoustic wave are what can be heard and seen during a lightning bolt in air.

Effects of High Voltage Electrical Discharges in Liquid Media

HVED can lead to biomolecule extraction only when occurring in a liquid media. HVED in liquids present some specific features that do not occur in a gas. These features will be discussed in this section and are illustrated in Fig. 6.

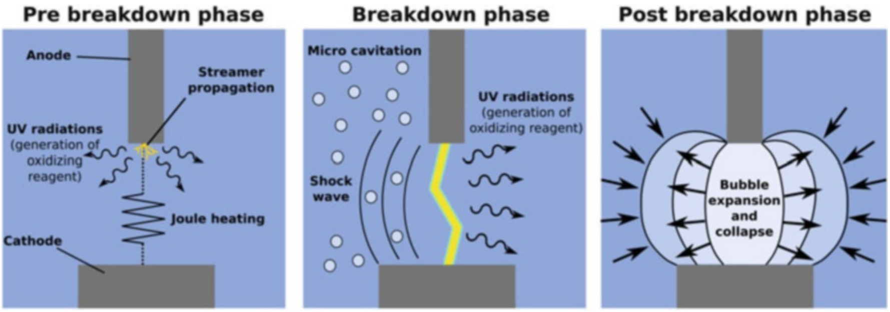


Fig. 6 Summary scheme of the main phenomena occurring during an HVED in water

Fragmentation of Raw Material

There are several phenomena that could possibly lead to the fragmentation of raw material. The role of each of these phenomena is not clear yet. It is possible to distinguish four of these, which will be described here in the chronological order.

The first phenomenon occurs when the streamer bridges the two electrodes, phenomenon that is sometimes called electrical breakdown. The temperature in the streamer reaches thousands of degrees in a few tens of nanoseconds, and the pressure reaches hundreds of MPa in the core of the plasma channel. Unlike a gas, liquids are to a large extent incompressible. When produced in a gaseous media, the electric arc creates an acoustic wave. In contrast, when produced in a liquid media, it leads to the formation of a powerful shock wave. This shock wave can reach hundreds of MPa in the vicinity of the streamer-liquid interface for a few microseconds. These shock waves have been measured and it has been showed that their intensity varies accordingly to the electric energy that pass through the electric arc and to the voltage at the moment of the breakdown (Touya 2003). The pressure measurement of a typical shock wave created by HVED in water is shown in Fig. 7, along with the voltage and electric current measurements.

The second phenomenon, which occurs when the liquid medium is water, is the apparition of very small microcavitation bubbles (diameter ~100 μm) directly following the shock wave. Figure 8 (Boussetta et al. 2013) shows pictures of HVED in water at different stages of the discharge. These pictures were taken with a fast aperture camera, and each image corresponds to a different discharge. The microcavitation bubbles can easily be seen on the second and third picture in Fig. 8. The first shock wave discussed above is immediately followed by a rarefaction wave, which pressure falls sufficiently far below saturated vapor pressure to cause the apparition of numerous small bubbles dispersed in the liquid. The causes leading to the apparition of these bubbles are similar to boiling, in the sense that

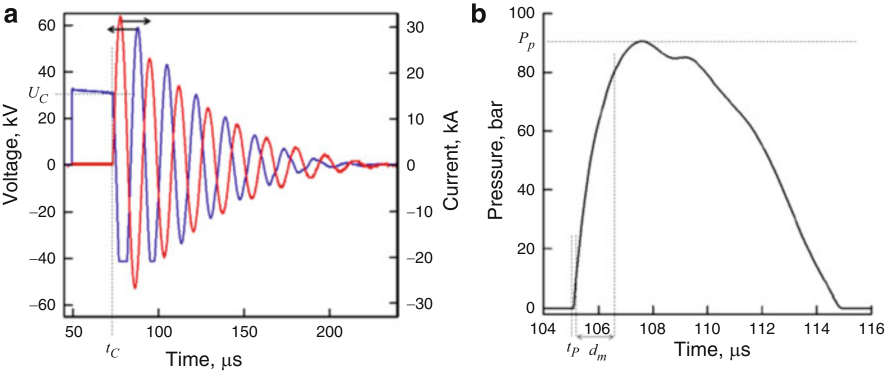


Fig. 7 (**a**) Variation of voltage and electric current during an electric discharge. U_c: breakdown voltage, t_c: Breakdown time. (**b**) Pressure variation during the first shock wave induced by an electric arc. P_p: maximum pressure, t_p: time of shock wave formation, d_m: rising time to maximum pressure (With permission from Boussetta et al. (2013))

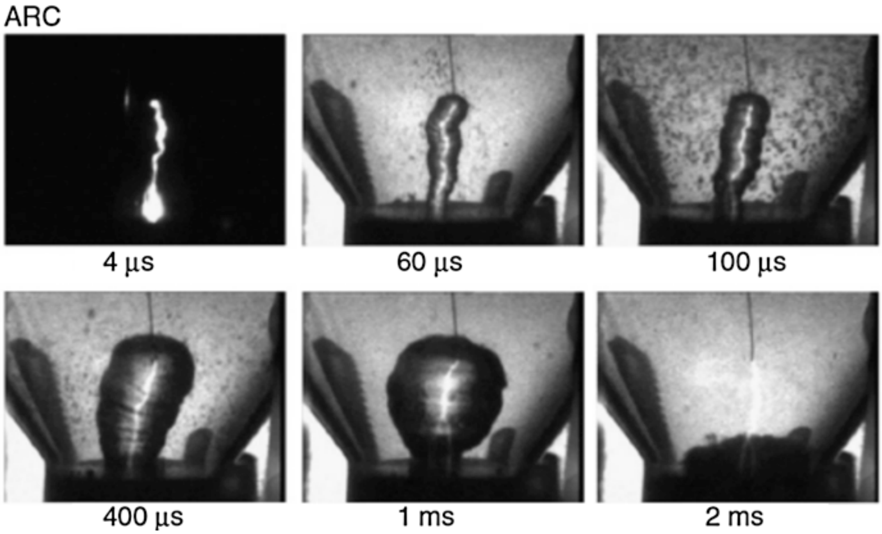


Fig. 8 Photographs of an electric arc in water taken at different delay after voltage rise. Each photograph corresponds to a different discharge. Voltage: 22 kV; Pulse energy: 1.6 J; interelectrode gap: 1 cm (With permission from Boussetta et al. (2013))

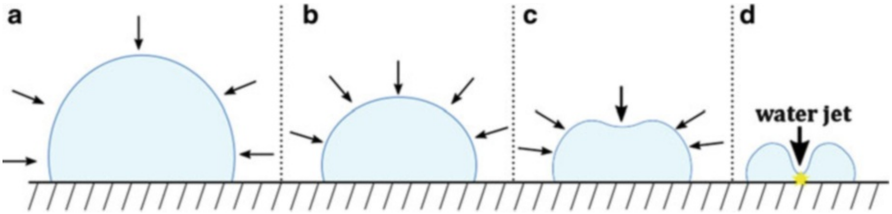


Fig. 9 Chronological evolution and collapse of a cavitation bubble in liquid, on a solid surface

phase transition from liquid to solid depends on the pressure and temperature conditions of the liquid. Usually, to achieve boiling, the pressure remains roughly stable while temperature rises. In this phenomenon of microcavitation, the temperature stays constant while the pressure quickly drops, leading to the formation of bubbles filled with very low-pressure vapor gas. Once the rarefaction wave is passed, the pressure of the medium goes back to normal and thus becomes much higher than the pressure inside the bubble. This causes bubbles to collapse and create intense and very localized shock waves. Close to liquid/solid interfaces, the collapse will occur via the mechanism known as “water jet.” The principle of water jet is showed in Fig. 9. In final stages of the bubble’s collapse close to a solid surface, the spherical shape of the bubble becomes unstable, and will tend to adopt the shape seen in Fig. 9c, where a water jet hits the opposite side of the bubble at high speed. These phenomena are well known to cause serious damages to engines working in aqueous media, like boat propellers, or gear pumps. It is suspected that microcavitation bubble collapse on the solid surface of grape seeds can lead to their fragmentation.

The third phenomenon, which occurs on a longer time scale, is the expansion of the post-breakdown bubble. The plasma channel and the vapor surrounding it are after the breakdown at very high temperature and pressure. This gaseous phase will expand until pressure equilibrium is achieved between vapor and liquid phase. The expansion of the gaseous phase is illustrated in Fig. 8, from the second to the fifth picture. The volume of the bubble resulting from this expansion depends on the electrical energy spent in the electric arc. In the experiment conducted by Boussetta and Lesaint (Boussetta et al. 2013), with a point anode of 200 μm radius spaced out 1 cm from the cathode (plane electrode), a voltage of 22 kV applied to the anode, and a small energy of 1.6 J, the bubble attains its maximum radius (12 mm) in 1 ms. Much larger radii and durations can be attained at higher energy. This expansion leads to violent hydrodynamic turbulence within the liquid, which can be the cause of raw material dispersion.

The last phenomenon that could also contribute to the raw material fragmentation is the collapse of the post-breakdown bubble discussed above. The mechanism of this collapse is similar to microcavitation, but the resulting shock wave is far stronger, since the bubble volume is several orders of magnitude greater. This shock wave can also contribute to raw material fragmentation, even though few studies have successfully measured it (Buogo and Cannelli 2002).

Electroporation and Joule Heating

The apparition of the electric arc, or in other word the electrical breakdown, does not occur instantaneously after the application of high voltage. Depending on the nature of the medium and on the electric field strength between the electrodes, the phase preceding the breakdown (pre-breakdown phase) can last from hundreds of nanoseconds to milliseconds. During this pre-breakdown phase, presence of high voltage in the liquid media creates the same effect as pulsed electric field. The first visible effect is joule heating. Anions and cations are set in motion under the influence of the electric field, and cause the heating of the media through their collision with neutral molecules. The dissipated energy during the pre-breakdown phase is largely responsible of any temperature rise that can be observed after an electric discharge treatment.

The other effect of the pre-breakdown phase is electroporation, which occurs in the same way that in regular pulse electric field treatment, except that in the case of electric discharge the duration of the high voltage pulse is not fully controlled.

Chemicals Generation

The electric arc generates a large variety of chemical reactions. This property of electric discharges has been and still is extensively studied, mostly for depolluting applications. The main source of chemical reaction is the intense electromagnetic radiations emitted by the arc. The peak of emission locates within the vacuum UV domain (100–200 nm), which is very energetic. The water absorbs the V-UV radiations and this leads to a large number of chemical reactions. Typical chemical

Table 2 Typical reaction rate constants for liquid-phase electrical discharge reactors (Locke et al. 2006)

Reaction	Reaction rate constant	Reference source(s)
Radical information $H_2O \rightarrow H + OH$	10^8–10^{-10} M s^{-1}	8, 18
Radical–molecule reaction $OH + \text{organic} \rightarrow \text{products}$	10^9–10^{-10} M^{-1} s^{-1}	127
Photochemical reactions (natural water) $^1O_2 + \text{organic} \rightarrow \text{products}$	(pH dependent) 10^6–10^8 M^{-1} s^{-1}	375
Electron–molecule $e_{aq}^- + H_2O_2 \rightarrow OH + OH^-$	10^{10} M^{-1} s^{-1}	380
Fenton's reaction $Fe^{2+} + H_2O_2 \rightarrow OH + OH^- + Fe^{3+}$	10^2 M^{-1} s^{-1}	118
Ozone–molecule $O_3 + \text{organic} \rightarrow \text{products}$	(pH dependent) 10^{-2}–10^4 M^{-1} s^{-1}	127
Aqueous electron reaction $e_{aq}^- + \text{chloroform} \rightarrow \text{products}$ $e_{aq}^- + \text{benzene} \rightarrow \text{products}$	10^{10} M^{-1} s^{-1} $<10^7$ M^{-1} s^{-1}	270 270

From radiation chemistry and other sources

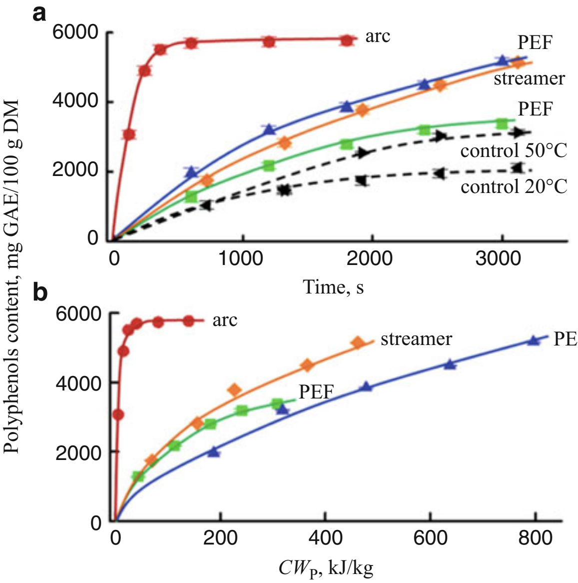
reactions caused by electric discharges are given in Table 2 (Locke et al. 2006). The main products of these reactions are extremely reactive oxidizing agents like hydroxyl radicals, hydrogen peroxide, and ozone. It is suspected that the generation of these oxidizing agents may degrade the extracted polyphenols.

Extraction of Polyphenol from Grape Seeds

Boussetta et al. have investigated the use of HVED for polyphenol extraction from grape seeds. In these studies, the raw matter (grape seeds) was mixed with water inside a closed treatment chamber, in which electrodes were immersed. A number of electric pulses were then applied to these electrodes generating electric arcs inside the grape seeds and water mixture. Through this process the polyphenols were extracted from the grape seeds. The effect of HVED has been compared to PEF treatment and simple solid–liquid extraction in water with no organic solvent addition (see Fig. 10) (Boussetta et al. 2013). HVED treatment both increases the yield and energy efficiency and drastically reduces the extraction time. HVED, PEF and grinding have been compared as pre-treatment followed by diffusion in a water ethanol solvent, with the ethanol added before or after the treatment. With ethanol added after the pre-treatment, grinding was the most efficient followed by HVED (Boussetta et al. 2012). When ethanol is added before the pre-treatment, results show that grinding and HVED are both equally effective.

In another study by Boussetta et al., the effect of HVED treatment duration has also been investigated for grape pomace (Boussetta et al. 2011). It was always observed that extraction versus time goes through a maximum. Beyond the optimal treatment time, the polyphenol yield decreases (see Fig. 11a). This phenomenon has

Fig. 10 Measured polyphenol content for control samples and treated samples by arc, pulsed electric field, and streamer: (**a**) versus treatment duration (or diffusion time for control samples), (**b**) versus cumulated energy input CW_p, per mass unit (With permission from Boussetta et al. (2013))



been observed in other studies (Liu et al. 2011). It seems that electrical discharges may degrade phenolic compounds, and that at the beginning of the treatment this effect is counterbalanced by the very fast extraction of polyphenols. In the same study by Boussetta et al., an HVED treatment has been performed on model solutions of catechin for different pH (see Fig. 11b). The degrading effect of discharges is confirmed. It is also observed that lower solvent pH slows down the catechin degradation and that a solvent with a pH = 2 even completely preserve catechin from degradation.

Material Used to Achieve High Voltage Electrical Discharges

The two key devices necessary to perform high voltage electrical discharges are the electrodes and the pulsed power generator. The influence of the treatment cell geometry, whether for a continuous or batch treatment, will not be discussed here due to the lack of studies on the subject.

The Electrodes

The electrodes geometry is a critical parameter for the efficient and reliable formation of electrical discharges. The geometry has a marked influence on streamer initiation and propagation, which both determine the formation of the electric arc. By changing the electrodes geometry, it is possible with the same electrical pulse to perform either pulsed electric field (without discharge) or HVED. The main adjustable parameters are the electrode shapes and the interelectrode distance.

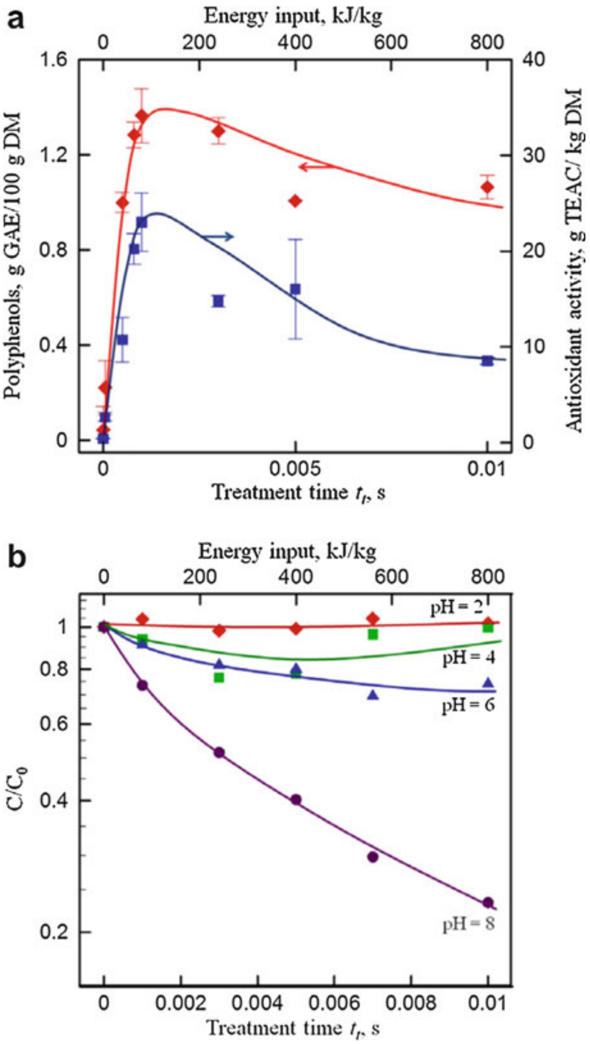


Fig. 11 (**a**) Effect of HVED energy input on total polyphenols yield and antioxidant activity. (**b**) Effect of HVED energy input on a model solution of catechin ($C_0 = 10$ mg/L in phosphate/citrate buffer solution, $T = 20$ °C) (With permission from Boussetta et al. (2011))

The influence of the interelectrode distance is easy to explain, as a smaller distance will result in a higher electric field between the electrodes. For example, in an ideal plane-to-plane geometry, the electric field is simply calculated by dividing the electric potential by the distance between electrodes. The other aspect is that the distance the streamer has to travel to induce an electric arc is the interelectrode distance, which means that breakdown will occur faster and using less energy with a smaller distance.

Concerning the electrode shape, the ideal geometry to achieve electrical discharges is point to plane, as shown in Fig. 12d. The point electrode is connected to the generator which delivers positive high voltage pulses, and the plane electrode is connected to the ground. The advantage of using a point electrode with a small tip

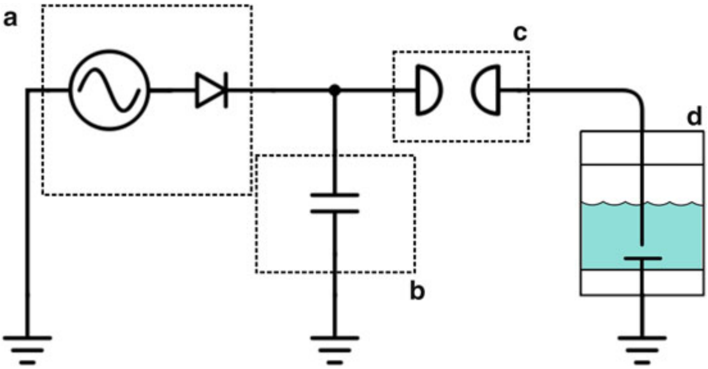


Fig. 12 Schematic representation of a basic generator (pulsed power generator). (**a**) High voltage power supply, (**b**) high energy storage capacitor(s), (**c**) high voltage switch (spark gap), (**d**) treatment chamber

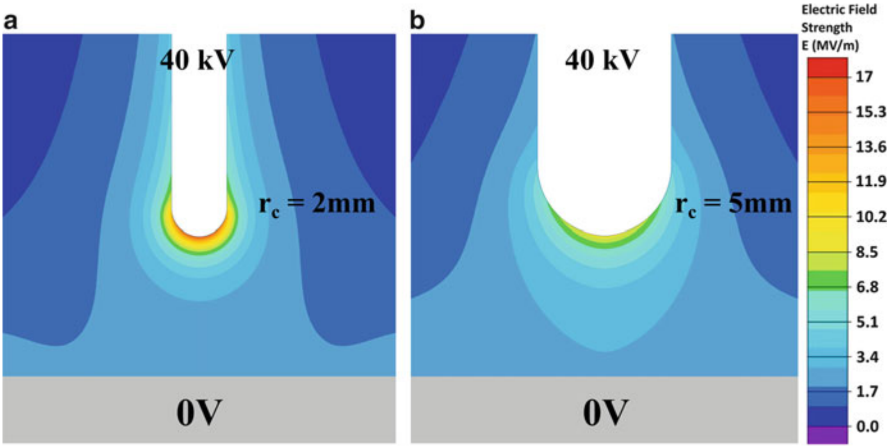


Fig. 13 Illustration of the point effect: simulation of the electric field strength of point-to-plane electrode geometries. The electrodes are immersed in water ($\varepsilon = 80$; $\sigma = 0.5$ s/m) and an electric potential $U = 40$ kV is applied on the point electrode. The curvature radius of the point electrodes are (a) $r_c = 2$ mm and (b) r_c =5 mm. Images obtained with an electrostatic simulation software (Quickfield professional 6.0)

radius of curvature is the large enhancement of the electric field occurring at the point tip. Figure 13 presents a numerical simulation illustrating this effect. When an electric potential of 40 kV is applied to points with spherical tips (5 and 2 mm radius of curvature), the maximum electric field obtained at the point extremity are respectively 9 MV/m and 15 MV/m. Using a very sharp point (radius about 0.1 mm) will greatly favor the initiation of streamers that appear immediately after the voltage rise (Boussetta et al. 2013). However, a major disadvantage of using very thin electrodes is that erosion, which is important with high energy discharges, will rapidly alter the geometry after only a few discharges. In contrast, a larger electrode radius (i.e., a rod) would maintain its geometry much longer. Conversely, the streamer initiation will be less easy, and will occur in water after a time delay that may last up to some 10 μs (Adda SFE). Consequently, a rod-to-plane electrode geometry will be preferred in applications that require a repeated use of high energy discharges.

Pulsed Power Generator

The simplest and most common kind of pulsed power generator is based on a capacitive discharge (see Fig. 12). Such generators include basically three parts: a high voltage power supply (Fig. 12a), one or several energy storage capacitors (Fig. 12b), and a high voltage switch (Fig. 12c). The high voltage supply is connected to the capacitors. The capacitors are connected to the high voltage switch, which is open during the capacitor charge in order to disconnect it from the treatment chamber (Fig. 12d). The electrical energy provided by the power supply is first stored in the capacitors. The high power switch is then closed, and all the electrical energy stored in the capacitors is delivered to the treatment chamber.

A capacitor has two main characteristics: its capacitance (C in Farads) and its maximum working voltage, which is the maximum voltage that the capacitors can handle. The energy stored in the capacitor can be calculated knowing these characteristics by the following formula:

$$E = \frac{1}{2} C V^2 \tag{1}$$

With E being the stored electrical energy (Joules), C being the capacitance (Farads), and V the charging voltage across the capacitors.

The high voltage switch is very often a “spark gap.” A spark gap is composed of two spherical electrodes in ambient air separated by some gap distance. These two electrodes act as an open switch as long as the voltage remains below a threshold value: the breakdown voltage of the air gap. When the voltage reaches this value, an electric arc occurs in air, and the spark gap is now similar to a closed switch. It is possible to control the threshold voltage by bringing the electrodes closer (which would lower the threshold) or farther (which would raise it). For a spark gap operating in a controlled gas pressure, the threshold can also be controlled by changing the gas pressure (the higher the pressure, the higher the threshold).

During operation, the power supply first charges the capacitors. The voltage rises alongside with stored electric energy following Eq. (1). When the threshold voltage of the spark gap is reached, it closes suddenly. In this way, the voltage between electrodes in the treatment chamber rises steeply, going from 0 to high voltage in nanoseconds.

Afterwards, the air discharge in the spark gap will remain as long as there is an electric current going through. This switch will open up only when the voltage roughly goes back to zero, i.e., when almost all the energy stored in capacitors is transferred to the treatment chamber. Hence, this kind of switch cannot provide square pulses, unlike other high voltage switches (i.e., transistor switches) that can open and close on demand. Since the capacitor is discharged in the chamber, the actual shape and duration of the applied voltage pulse depend on the current flowing through the chamber, which in turn depends on several parameters such as liquid conductivity and gap distance.

Streamers

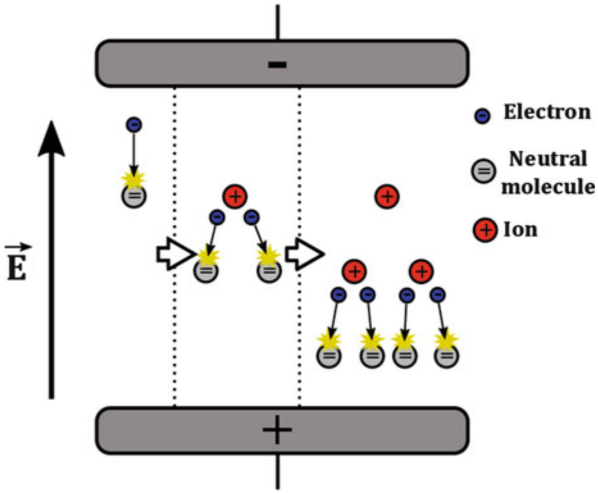
A streamer is a term referring to the phase preceding the formation of the electric arc. More precisely, it relates to the formation and the propagation under a high electric field of a "cold" plasma channel from the tip of the high voltage electrode toward the grounded electrode in a dielectric media. In liquids, the plasma channel is hot and the correct term for this phenomenon is "leader," but the distinction is often ignored. Here the term "streamer" will stand for both streamers and leaders, for simplification purposes. The focus will be put on streamers generated with voltage of positive polarity (called "positive" streamers), since the propagation of negative streamers in water is much more difficult and requires higher voltage.

The streamer physics is somewhat complex and sometimes counterintuitive. Understanding streamer physics can help predicting the formation of electric arcs and avoiding common mistakes. For instance, a mistake often made is to misinterpret the role of the media's electrical conductivity on breakdown. Indeed, an electrical discharge can be generated at lower voltage in air than in water, even though water is considerably more conductive than air. On the contrary, in similar conditions, discharges cannot occur in hydrocarbon oils, which are very good insulator but can occur in salted water. Conductivity in most cases does not represent an adequate parameter for discharge generation and propagation. Other parameters such as density explain the large difference between liquids and gases, or permittivity that explains the large difference between oil and water. In liquids, except in extreme conditions, a discharge can only occur after a phase transition from liquid to gas. Before describing the different aspects of streamers in water, the role of the medium's density will be illustrated by explaining the ionization mechanism known as "electron avalanche."

Electron Avalanches

Electron avalanche (frequently called "Townsend" avalanche) is the main physical phenomenon causing the ionization of the neutral gas, changing it into conductive plasma. The mechanism of electron avalanches is illustrated in Fig. 14. When exposed to an electric field inside a dielectric media, a free electron is accelerated toward the positive electrode until it collides a neutral molecule. If the accelerated electron has enough kinetic energy, this collision will tear one electron from the neutral molecule. The result of such a collision will be one positive ion (the former neutral molecule) and two electrons: the one that collided and the one that has been ripped from the neutral molecule. The same process repeats with the two electrons, resulting in two more positive ions and two more electrons, and its further repetition

Fig. 14 Schematic representation of an electron avalanche's first steps



leads to an exponential rise of ionization and charges. This mechanism basically shows how a gas is ionized to eventually form a streamer.

The primary condition for this mechanism to take place is that between two collisions, the electron is accelerated enough to reach ionization energy. This mainly depends on two simple parameters: the electric field strength, and the average distance an electron can travel freely before colliding (mean free path, MFP). For a longer MFP, the electron accelerates for a longer time between two collisions and gathers more kinetic energy. The MFP definition is

$$l_{\mathrm{MFP}} = \frac{1}{\sigma n} \tag{2}$$

Where σ is the surrounding molecule's cross section (the surface of molecules "seen" by the electron), and n the density of the medium. In air at atmospheric pressure, the typical value for MFP is 68 nm. Liquid water being much more dense, the MFP is considerably smaller and estimated to about 0.2 nm. Thus, in liquid water a free electron should not accelerate enough to ionize a neutral molecule, unless a very high field is present (about 10 MV/cm). That is why a discharge can occur at much lower voltages in air than in liquids. This also explains that in liquids, streamers initiation and propagation are almost always preceded by liquid to gas phase transition.

Streamers in Water

The streamer ignition and propagation mechanisms are well known in gases. However, the ionization of the gas mainly relies on electron avalanches, which are virtually inexistent in liquids. In liquids, a liquid to gas phase change has to occur prior to streamer inception and propagation. Therefore, streamers result from a combination of multiple physical mechanisms leading to phase transition and ionization, making this phenomenon very complex. It is not as well understood as in gases, and there are still no predictive models of electrical breakdown in liquids. Illustrations of streamers in liquids can be seen in Fig. 15b and c.

Studies have also shown the existence of several streamer "modes," influenced by experimental factors like the applied voltage, the electrode geometry, the nature of the liquid, and the hydrostatic pressure (Lesaint 2016). The different streamer modes show different propagation velocities and shapes. A diagram of the different streamer modes in water, as a function of voltage in a 3 cm point-plane gap, is presented in Fig. 15a.

The "first mode" streamer, also called "subsonic" streamer, appears at the lowest voltage and gets the lowest propagation velocity. This mode has been observed in Adda et al. (2016), at relatively low voltage ($U = 2$–10 kV, anode radius $= 0.6$ mm) in water of different conductivities ($\sigma = 5$–1000 μS/cm). With these conditions, the inception of the streamer is always preceded by the formation of a vapor bubble, and the streamer ignites as discharges occurring inside this vapor bubble. The vapor bubble is initially formed because of the Joule heating nearby the anode due to the water conductivity, and it appears once the water reaches boiling temperature. Hence, the streamer inception in these conditions greatly depends on the energy spent by Joule dissipation, and hence on the liquid's conductivity. Once the streamer starts inside the bubble, the vapor cavity expands in a bush-like pattern, as seen in Fig. 15b.

When the applied voltage is raised, a second mode appears, much brighter, with a filamentary shape, and a much faster velocity (see Fig. 15c). This mode is also called "supersonic," and has a velocity from 0.5 to 2 km/s. Different modes can be observed successively when a streamer propagates. This is illustrated in Fig. 15b, where 16 kV is applied to a 1.2 mm diameter anode in 200 μS/cm water. In this picture, a first subsonic streamer is seen transforming into a supersonic streamer, considerably brighter with a filamentary shape.

A third and fourth mode also appear at even higher voltages. The streamer's propagation velocity can then reach 30 km/s (Fig. 15a). The physical mechanisms responsible for these transitions from one mode to another are not well known yet, and few studies have been conducted on these matters due to the extreme conditions (voltage, pressure, temperature) in which these phenomena occur.

Considering the conditions used in extraction experiments such as Fig. 11 (40 kV, 5 mm gap distance), the streamer mode involved in the breakdown process of water should be of the fourth mode. However, the transposition of results obtained in water alone to the case of extraction experiments should be made with great care. If dry grape seeds containing air pockets are present in water, breakdown within air pockets should first occur (see above), and this possibly could modify the initiation of breakdown compared to the case of water alone (shorter time to breakdown are measured in this case). Other experiments also showed that the presence of extraction by-products (presumably polyphenols) induced a reduction of the streamer propagation velocity compared to water alone (Boussetta et al. 2013). Altogether, these results show that pre-breakdown phenomena actually involved in extraction experiments cannot be simply transposed from results obtained in water alone.

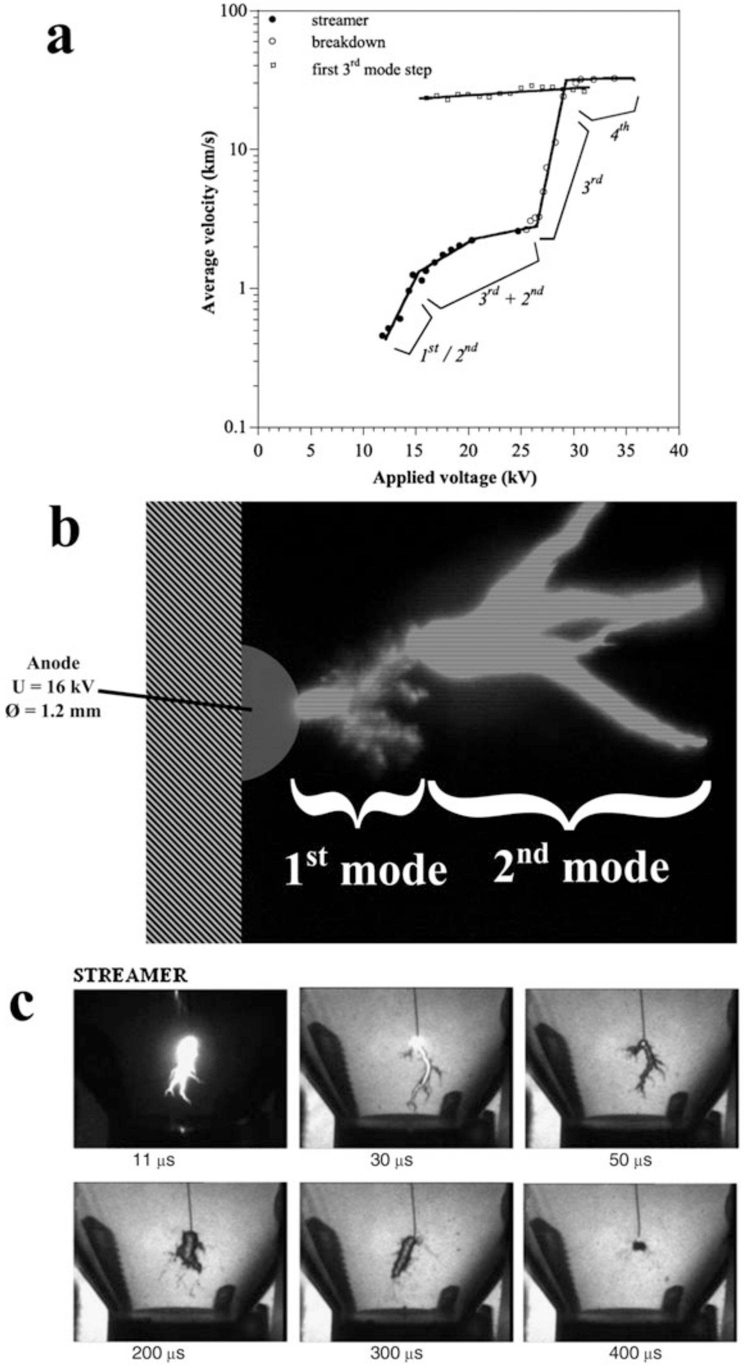


Fig. 15 (**a**) Average streamer propagation velocity as a function of applied voltage (With permission from Lesaint (2016)), (**b**) mixed first and second mode streamer image. Unpublished data

Conclusions

Conventional liquid–solid extraction has shown to be an effective way of extracting phenolic compounds from grape seeds. Use of specific solvent like ethyl acetate can even selectively extract some polyphenols. However, to get the maximum yields, it is necessary to have a rather long extraction time (from 1 to 24 h), even if the solid–liquid mixture is heated. The use of electrotechnologies, and especially HVED, constitutes another means of extracting polyphenols from grape seeds with a greatly enhanced efficiency and speed. HVED combines PEF features (electroporation) with the mechanical disruption of the seeds, leading to a quick extraction of polyphenols contained in the inner parts of the seed. The drawbacks of this technique are that the extraction is not selective, and also that overusing HVED may lead to a degradation of polyphenols. The high voltage pulsed power generator can also be dangerous and requires special security procedures, and the phenomena leading to the extraction are complex and not totally understood. This chapter has hopefully given the basic knowledge to start working efficiently with HVED. Yet, further studies on the physics of discharge in liquids, and especially on physical phenomena related to seed disruption (shockwaves, bubble dynamics), are necessary to obtain a better control of this process and to transfer this technology to larger scales.

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Fig. 15 (continued) obtained in the same conditions as Adda et al. (2016), in water with a conductivity $\sigma = 200$ μs/cm. (**c**) Photographs of a fourth mode streamer in water taken at different delay after voltage rise. Each photograph corresponds to a different streamer. Voltage: 17 kV; Pulse energy: 1.9 J; interelectrode gap: 1 cm (With permission from Boussetta et al. (2013))

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