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A study of mechanisms involved during the extraction of polyphenols from grape seeds by pulsed electrical discharges

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ABSTRACT

This paper presents an experimental study of the influence of pulsed electrical discharges of low energy (3 to 10 J) on the extraction of polyphenols from grape seeds. To obtain a better understanding, three basic phenomena involved in the whole discharge process are studied separately: pulsed electric field (PEF), pre-breakdown phase (streamer), and breakdown phase (arc). The polyphenol extraction is much more efficient with arcs, compared to streamers and PEF. Therefore, during the discharge process, the enhancement of polyphenol extraction can be mainly ascribed to the final arc phase. The total energy per unit mass CW_p required to extract 5000 mg GAE/100 g DM with the arc ($CW_p = 16$ kJ/kg) is 27 times lower compared to streamers alone, and 47 times lower compared to PEF. An optical study shows that the mechanical effects of arcs (shock waves, expanding cavity, and strong turbulence) are much more pronounced compared to streamers. These mechanical effects are responsible for the fragmentation of grape seeds, and strongly promote the release of polyphenols. Other parameters such as the test cell shape and the inter-electrode distance also show that the polyphenol extraction is further enhanced when grape seeds are in close proximity with the breakdown arc. In optimized conditions, the extraction efficiency with low energy discharges can be significantly higher than previous measurements with high energy discharges.

Industrial relevance: This paper presents relevant information for the design of generating electrical discharges treatment. The study also addresses a specific case of use of by-products and shows the effectiveness of such technology.

1. Introduction

Grapes are one of the fruit crops grown widely in many areas of the world and 46% of the fresh grapes produced are accounted for in wine production (Anonymous, 1999). During winemaking, large quantities of grape pomace are produced as a by-product (Ohnishi, Hirose, Kawaguchi, Ito, & Fujino, 1990). Grape seeds comprise 38 to 52% of the pomace (dry matter basis) (Kamel, Dawson, & Kakuda, 1985). Grape seeds are a rich source of natural antioxidants called polyphenols. Upgrading of this typical low-value food by-product can be useful for the production of polyphenol extracts, functional food components, useful health ingredients and antioxidant additives.

The industrial extraction of polyphenols is performed with a mixture of alcohol and water. However, a rather long diffusion time (3–20 h) is required for the extraction (Boussetta, 2010). Recently, electrotechnologies (in particular high voltage pulsed arcs) have been shown to induce physical and chemical processes acting on cell tissue and enhancing the release of intracellular compounds (Boussetta, Reess, Vorobiev, & Lanoisellé, 2011). When combining an electrical pretreatment and a diffusion process, the total extraction time is reduced compared to an extraction without electric treatment (for similar final extraction yield) (Boussetta et al., 2009, 2011). Physical processes due to the pulsed arc include the formation of ultraviolet light (Locke, Sato, Sunka, Hoffmann, & Chang, 2005) and shock waves (Boussetta et al., 2012; Touya, 2003), which both depend on the discharge energy. Chemical processes are also induced by electrical discharges in water: formation of reactive radicals and molecular species such as hydrogen peroxide and ozone (Dang, Denat, Lesaint, & Teissedre, 2008; Dang, Denat, Lesaint, & Teissedre, 2009; Locke et al., 2005).

Electrical discharges have been studied as a means for cell disruption in biochemistry, biology, medicine and drug delivery (Akiyama, 2000; Sunka, 2001), and bio-compound extraction from different products (Boussetta et al., 2009; Boussetta, 2010; Boussetta et al., 2011; Gros, Lanoisellé, & Vorobiev, 2003). In previous studies, they have been successfully applied on the laboratory scale to grape pomace, grape skins, grape stems and grape seeds to intensify the

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polyphenol extraction (Boussetta, 2010). The same tendency has been observed at the pilot scale (Boussetta, Vorobiev, Reess, et al., 2012). These studies have dealt with the application of strong electrical discharges (energy of ~200 J/pulse), but electrical discharges of lower energy (1–10 J/pulse) have not yet been studied for polyphenol extraction. The physical effects of electrical discharges in an aqueous suspension of bioproducts are not yet well understood.

The aim of this work is to study the effects of electrical discharges of low pulse energy (<10 J) on the extraction of polyphenols from grape-seeds. In order to obtain a better understanding, three basic phenomena involved in the whole discharge process are studied separately: pulsed electric field (PEF), pre-breakdown phase (streamer), and breakdown phase (arc). The main features of streamers, arcs, and PEF are first characterized in the water alone: typical currents, energy, and thermo/mechanical effects (shock wave and cavity expansion). Then, experiments carried out with grape seeds are presented, with the objective to determine the energy efficiency of extraction with pulsed streamers, arcs, and electric field.

2. Materials and methods

2.1. Biological material

Industrial grape pomace of *Vitis vinifera* var. Pinot Meunier from Epernay (France) was obtained as the residue of pressed grapes. Grape seeds were then separated from grape pomace. Grape seeds were industrially dried in a hot air dryer with a residence time of 15–20 min and then collected for analysis. The mean diameter of the grape seed is 4 mm. The dry matter content of dried seeds is 93 ± 1%.

2.2. Test set-up for pulsed electrical arcs (set-up A)

The principle of the experimental set-up A is described in Fig. 1. In order to generate pulsed arc discharges in water, a point-plane gap was used, constituted by a tungsten wire (200 μm in diameter) emerging from a PTFE (polytetrafluoroethylene) holder, facing a stainless steel plane electrode. The tungsten wire, eroded by repeated discharges, was periodically renewed. The inter electrode distance *d* was adjusted from 1 to 3 cm.

Two different shapes of test cell were used (Fig. 2). In the cylindrical cell (Fig. 2a), grape seeds lay on a 50 mm diameter grounded electrode. In the cylindro-conical cell (Fig. 2b), the diameter of the grounded electrode was reduced to 20 mm. The conical part of the cell body tends to concentrate grape seeds in the discharge region. The cell body made with transparent PMMA (polymethyl-methacrylate) allows the direct observation during the experiments. The maximum volume of the cylindrical test cell is 250 ml, and 80 ml for the cylindro-conical cell.

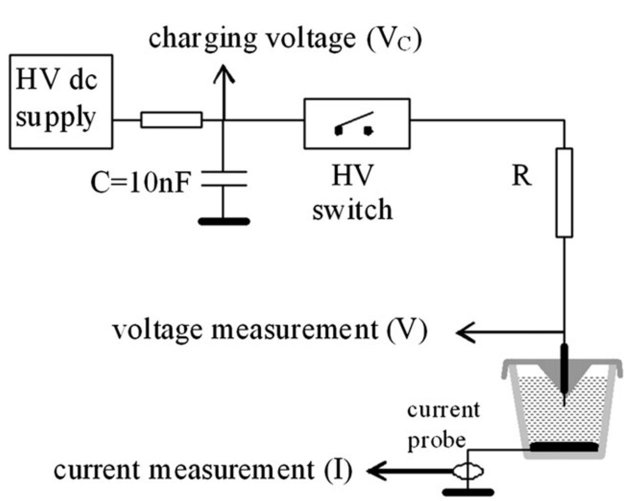

Fig. 1. Experimental set up used to generate pulsed arcs in water.

To generate repetitive high voltage pulses, a fast semiconductor high voltage switch is used instead of the classical spark gap (Fig. 1). This electronic switch is based on a stack of thyristors, allowing switching high voltage up to 60 kV at a maximum current of 1 kA. The thyristor switch operates basically as a spark gap: it remains closed until the capacitor *C* is fully discharged. To protect the electronic switch, a resistor *R* (10 to 47 Ω) was placed in series in order to limit the arc current below the 1 kA limit. In turn, this resistor has an influence on the discharge process. In this study, the resistor *R* was varied in order to measure its effect on the polyphenol extraction yields, and the corresponding shapes of transient voltage and current during treatment.

The voltage *V* on the test cell is recorded with a fast high voltage probe (75 MHz bandwidth), and the current *I* with a Rogowski transformer (20 MHz bandwidth). From the measured voltage $V(t)$ and current $I(t)$, the instantaneous power $P(t) = VI$ is calculated numerically, and the total dissipated energy per pulse W_p is obtained by integration of the power *P* for the whole duration T of the pulse (Eq. (1)).

$$W_p = \int_0^T V(t)I(t)dt. \tag{1}$$

2.3. Extraction experiments with pulsed arcs

The treatment cell was initially filled with grape seeds (1.75 g) which were then mixed with distilled water at room temperature. The liquid–solid mass ratio was fixed at 40. Depending on the experimental conditions, the pulse energy Wp was in the range 3–10 J (and the corresponding specific pulse energy was in the range 41.8–139.4 J/kg). Electric arc treatment consisted in applying up to 1800 successive pulses with a repetition rate of 2 Hz. This frequency was chosen in order to induce a moderate increase of the solution temperature (typically 10 °C after 2000 pulses). The total treatment time lasted up to 15 min. The treatment was stopped at regular intervals for about 5 min, and samples were taken in order to measure the total polyphenol content, temperature and conductivity. During experiments, the conductivity increased from the initial 18 μS/cm value, up to 350–450 μS/cm at the end of the treatment (depending on the operating conditions).

At each shot, a violent motion of water and grape seeds was observed, and a rapid fragmentation of seeds occurred. Fig. 3 shows pictures of the test cell before and after the treatment. Seeds are finely ground, and the solution becomes of light brown color, containing a large amount of fine particles in suspension.

2.4. Test set-up for measurements with streamers and pulsed electric field (set-up B)

In order to carry out experiments with streamers only, avoiding the electrical arc, we used the following materials and conditions, derived from a previous study of discharges in water (Dang et al., 2008, 2009). The gap distance of the point-plane cell was increased to $d = 3$ cm, and the thyristor switch was replaced by a MOS (metal oxide semiconductor) switch. Compared to the thyristor, the MOS allows switching off the voltage before the capacitance is totally discharged. High voltage pulses of 0.8 μs duration were produced with this system. During this short time, pre-breakdown streamers with a velocity 30 km/s are unable to reach the opposite electrode at a gap distance $d = 3$ cm, and no electric arc can occur.

Pulsed electric field experiments (PEF) were carried out with the same set-up B, by replacing the point electrode by a plane electrode (25 mm diameter) placed at a distance $d = 1$ cm from the grounded plane (Fig. 2c).