Accepted Manuscript

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PII: S0924-2244(16)30520-9

DOI: 10.1016/j.tifs.2017.05.016

Reference: TIFS 2018

To appear in: *Trends in Food Science & Technology*

Received Date: 15 November 2016

Revised Date: 4 February 2017

Accepted Date: 23 May 2017

Please cite this article as: Botero-Uribe, M., Fitzgerald, M., Gilbert, R.G, Midgley, J., Effect of pulsed electrical fields on the structural properties that affect french fry texture during processing, *Trends in Food Science & Technology* (2017), doi: 10.1016/j.tifs.2017.05.016.

Effect of pulsed electrical fields on the structural properties that affect french fry texture during processing

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This work was funded by the Australian Research Council, IRTP Scheme with Grant Number IC130100011.

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Abstract

Background:

The french-fry manufacturing process via frozen partially-prepared fries involves a series of heat treatments in which the structural properties of a potato (starch structure, ion content, water content, cell wall architecture, and middle lamella) are substantially altered to produce a french fry with a crispy crust and a mealy core. In addition to the traditional processing steps (washing and sorting, peeling, cutting, blanching, dipping, pre-drying, par-frying and freezing), short pulses of high voltage (pulsed electric field, PEF) are now often applied to potatoes before they are cut into french-fry strips. The final texture is the result of not only the effects of heat and PEF treatments on the structural properties of the potato tuber, but also the effects of interactions between these treatments.

Scope and approach:

This paper explains the main processes involved during manufacturing of french fries and their effect on the tuber structure properties responsible for french fry texture (changes in starch structure, cell wall architecture, water and oil content) currently available. It summarizes the research on the effect of PEF on those structural properties, their relevance, and applicability and highlights future research needs.

Key findings and conclusions:

The effect of heat treatments (steam peeling, blanching, pre drying, par frying) and freezing on the structural properties that affect texture have been widely studied. Manufacturers have adopted a new procedure, PEF treatment, about which little is known about the effect on the structural properties that affect texture and the synergistic interaction effects with the other manufacturing steps of french fry production. There is a need for investigation of these changes and the mechanistic reasons for any effects on final texture.

Key words: French fry; Pulsed electrical fields; frying; blanching

General Introduction

French fry texture

French fries exhibit two very distinct textures: a “crispy” crust, with similar physical characteristics to potato chips (often called crisps) (Pedreschi & Aguilera, 2002), and a “firm-mealy” core, with some of the textural properties of boiled potatoes. The crispy crust can be described as a semi-rigid sponge with 80% void space (Lima & Singh, 2001). It is made of shrunken cells with very low water content, and is usually 1-2 mm thick, varying with frying time and temperature (Sanz, Primo-Martín, & Van Vliet, 2007). The interior, or crumb, can be described in terms of firmness, mealiness, and waxiness (Andersson, Gekas, Lind, Oliveira, & Oste, 1994). 'Mealiness' is a term used to convey a granular mouth feeling on the tongue (Bettelheim & Sterling, 1955). A mealy cooked potato looks glistening in appearance, has a crumbed texture, and can easily be broken down, but keeps its shape (Andersson, Gekas, Lind, Oliveira, & Oste, 1994). French fries with a wet and pasty feel on the tongue (soggy texture) are usually not desired.

Potato Structural properties affecting texture

The major structural properties of the tuber that affect french fry crispness are moisture content, oil uptake and starch content and distribution along the tissues (Hoff, 1972). Other major factors that affect crispness relate to the manufacturing process — pre-drying and par frying conditions (Pedreschi, Moyano, Santis, & Pedreschi, 2007; Lisińska & Gołubowska, 2005; Kita, 2002).

Mealiness and firmness are affected by starch properties (molecular structure, amount and distribution within the tuber), cell size (Hoff, 1972), starch swelling pressure and gelatinization properties (Jarvis, Mackenzie, & Duncan, 1992; Hoff, 1972), as well as cell-wall polysaccharides and non-starch polysaccharides (Jaswal, 1991). Firmness is the result of three major changes that occur in the potato tuber as a consequence of the chemical, physical and structural changes occurring during the manufacturing process (Shomer & Kaaber, 2006; Thybo, Christiansen, Kaack, & Petersen, 2006): first, starch becomes gelatinized; next, cell walls are weakened with an accompanying increased permeability; last, intercellular adhesion between adjacent cells is reduced (Moyano, Troncoso, & Pedreschi, 2007; Van Marle et al., 1997; Andersson, Gekas, Lind, Oliveira, & Oste, 1994). The intensity of these changes

depends on thermal conditions, such as temperature and treatment duration during processing.

French fry manufacturing process

French fry manufacturing is a series of processes, namely washing and sorting, steam peeling, pulsed electrical field treatment, cutting into strips, blanching, dipping, pre-drying, par-frying and freezing (Fig.1). The processes that have the most significant effect on french fry texture will be considered here.

Steam Peeling

Potato skin is a layer of dead corky periderm cells, around 10 cells deep, that do not contain much starch or protein (Fedec, Ooraikul, & Hadziyev, 1977).

Removal of the potato skin by steam peeling allows high automatization, control of time and temperature, and high yield of potato. The high steam temperature used for peeling causes internal pressure to build, resulting in mechanical failure of the cell and reduction in cell turgor. These changes to the properties of the cells are due to the partial hydrolysis and degradation of pectin and other polysaccharides in cell walls and in middle lamella (Garrote, Silva, Bertone, & Avalle, 1997) . The potato layers close to the surface are the most affected by this heat treatment.

Pulsed Electrical Field (PEF) treatment

PEF treatment is basically an electrical stimulation with pulses of high intensity and short duration (Vorobiev & Lebovka, 2009) and is currently applied to plant cells to increase membrane permeabilization. A cell can be considered as a capacitor containing material of low dielectric constant (Raso-Pueyo & Heinz, 2010) and when electric fields are applied to it, the cell membrane amplifies these fields (Jemai & Vorobiev, 2002). PEF causes cell membranes (plasma membrane and tonoplast) to be electrically charged due to the accumulation of opposite charges on the two sides of the membrane and the movement of those charges through the membrane under the electric field. A transmembrane electrical potential is created due to potential difference across the membrane (Ho, Mittal, & Cross,

1997; Zimmermann, 1986). Cell membranes are generally very thin and do not need a strong electric field to create a transmembrane potential.

It is well known that conductivity in the membrane increases immediately after the pulsed treatment (Angersbach, Heinz, & Knorr, 2000) and the membrane becomes more permeable as the conductivity increases (Pereira, Galindo, Vicente, & Dejmek, 2009; Gómez Galindo, Vernier, Dejmek, Vicente, & Gundersen, 2008; Bazhal, Lebovka, & Vorobiev, 2003). This increase in membrane permeability seems to re-establish the equilibrium between the electrochemical and electrical potential differences between the cell plasma and the extra-cellular surroundings (Raso-Pueyo & Heinz, 2010). Electro-permeabilization of the membrane occurs when the normal cell transmembrane potential (60 to 110 mV) or "normal resting potential" (Weaver & Chizmadzhev, 1996) is exceeded.

Electric breakdown is the first stage of permeabilization, which is followed by an osmotic process at the interior of the cell, such as intracellular liquid release, diffusion of solutes, and resealing of membrane if the treatment is mild (Vorobiev & Lebovka, 2009; Zimmermann, Vienken, & Pilwat, 1980).

PEF has the unique property of causing selective damage to cells: the membrane has been shown to be the only part affected (Vorobiev & Lebovka, 2009), with the lipid portion being the site of the electric interaction (Weaver & Chizmadzhev, 1996). The total electric field in the membrane or the total membrane voltage determine the electric breakdown behaviour of the membrane (Zimmermann, 1986).

The degree of permeabilization depends on the cell membrane properties (size, conductivity, shape and orientation) and the electric pulse parameters (field strength, pulse amplitude, pulse shape, pulse duration and number of pulses) (Vorobiev & Lebovka, 2009; Kandušer, Šentjurc, & Miklavčič, 2008; Lebovka, Bazhal, & Vorobiev, 2001; Teissie, Eynard, Gabriel, & Rols, 1999). It is generally agreed that if the amplitude and duration of the treatment is not too high, the membrane returns from the state of high conductance to its initial state (Chernomordik et al., 1987). Under those conditions, the membrane can reseal, the viability of the cell is maintained (Guderjan, Töpfl, Angersbach, & Knorr, 2005), and metabolic activity can be restored (Pereira, Galindo, Vicente, & Dejmek, 2009). This is known as the "reversible electric breakdown' as the conductance of the cell is increased (Weaver, Powell, Mintzer, Sloan, & Ling, 1984). Small cells reach breakdown voltages at lower field strengths than those required for larger cells (Zimmermann, 1986). Reversible breakdown generally occurs when only a small portion of the membrane has pores (Knorr & Angersbach, 1998; Ho, Mittal, & Cross, 1997) or the pores remain small in comparison to the membrane area.

Irreversible breakdown is important if the cell vitality is to be maintained and the production of secondary metabolites is required (Raso-Pueyo & Heinz, 2010).

By increasing field strength, pulse duration and number of pulses, the density (number and size) of pores in the cell membrane and in the cell wall increases, and can cause rupture of the membrane (Asavasanti, Ristenpart, Stroeve, & Barrett, 2011; Pereira, Galindo, Vicente, & Dejmek, 2009; Gómez Galindo, Vernier, Dejmek, Vicente, & Gundersen, 2008; Arevalo, Ngadi, Bazhal, & Raghavan, 2004; Bazhal, Lebovka, & Vorobiev, 2003; Fincan & Dejmek, 2002; Knorr & Angersbach, 1998; Zimmermann, 1986). The cell may also be damaged by the overheating of the membrane surface, or chemical imbalances caused by transport out of the cell. Membranes can lose the ability to perform physiological tasks such as osmoregulation, due to loss of cytoplasmic fluid (Raso-Pueyo & Heinz, 2010). Irreversible breakdown is useful in processes, such as some of those in preparing french fries that require mass transfer as membranes lose their barrier function (Raso-Pueyo & Heinz, 2010).

Electropermeabilization brought about by electric current seems to induce the generation of reactive oxygen species as a cellular response to stress. An increase in lucigenin luminescence was seen after pulsing black Mexican sweet maize cells with field strength larger than 150 V cm^{-1} with a 15 ms single pulse (Sabri, Pelissier, & Teissie, 1996). These authors attributed the increase in the luminescence to generation of activated forms of oxygen as an oxidative stress response of the cells to the PEF treatment. As the field strength increased, the loss of viability decreased and cells were killed as the field strength approached 1000 V cm^{-1}. It was shown that the extent of electropermeabilization and loss of viability were linearly related to the reciprocal of field strength. However, no linear relationship between cell viability and chemiluminescence was found, suggesting that the stress reaction of the intact cells involves more than the electrically affected membrane. Similar results were obtained on the studies on potato cell viability in peeled and unpeeled potato using a water-soluble tetrazolium salt 0.5% (w/v) stain. A PEF treatment of 0.2 kV cm^{-1} did not kill the cells but when treatment reached a level of 0.6 kV cm^{-1}, all cells, including the outer medulla, lost their viability (Faridnia, Burritt, Bremer, & Oey, 2015). Living cells exhibited the red formazan colour resulting from the reduction of tetrazolium salt by the oxidoreductase enzymes. As the intensity of the field strength increased, the number of dead cells (not stained) increased, with the inner medulla and pith tissue being the most affected. The response of a cell membrane that was associated with induced permeabilization has also been studied (Gómez Galindo, Vernier, Dejmek, Vicente, & Gundersen, 2008). They

studied the effect of PEF application on the diffusion of a fluorescent dye (FM1-43) through the cell wall under field strengths of 30 – 500 V cm^{-1}) with a single 1 ms rectangular pulse. They concluded that mild PEF treatment had a similar effect to stress responses – peroxidase mediated oxidative cross-linking reactions – on plant cells.

PEF treatment is used commercially in the food industry due to its effect on enhancing diffusion processes and drying (Raso-Pueyo & Heinz, 2010; Vorobiev & Lebovka, 2009). PEF is used in the potato industry because research shows some promising results for reducing cutting forces, increasing drying rates, and mass transfer during frying lowering oil uptake (Janositz, Noack, & Knorr, 2011; Angersbach, Heinz, & Knorr, 2000).

Blanching

Blanching is a heat process widely used in the French fry industry, in which french fry strips are scalded in hot water. It is well established that during blanching, starch becomes partially gelatinized, cell walls are weakened with an accompanying increased permeability and intercellular adhesion between adjacent cells is reduced (Moyano, Troncoso, & Pedreschi, 2007; Shomer & Kaaber, 2006; Thybo, Christiansen, Kaack, & Petersen, 2006; Van Marle et al., 1997; Andersson, Gekas, Lind, Oliveira, & Oste, 1994). Blanching also deactivates enzymes, leaches out reducing sugars, and air is removed from tissues (Moyano, Troncoso, & Pedreschi, 2007; González-Martínez, Ahrné, Gekas, & Sjöholm, 2004). The intensity of these changes depends on temperature conditions during processing.

Potato starch makes up most of the dry matter (60-80%) in a french fry (Kita, 2002). Starch is a highly branched glucose polymer with (1□4)-α linear bonds and (1□6)-α branch point. The starch in an uncooked potato is arranged in multiple alternating crystalline and amorphous lamellae with ~ 9 nm spacing between each. Starch is made up of two types of glucose polymer with these linkages: amylopectin and amylose. Amylopectin is of very high molecular weight and contains relatively short chains (branches). It accounts for 70 – 80% (by weight) of potato starch, regardless of granule size (Yusuph, Tester, Ansell, & Snape, 2003). The weight-average molecular weight ($\overline{M}_w$) of potato amylopectin is typically ~ 7×10^7, with a broad distribution of molecular weights and sizes, and the radius of gyration (R_g) of the fully-dissolved molecule is ~225 nm (Aberle, Burchard, Vorwerg, & Radosta, 1994).

Studies on the chain-length distribution (the number of glucose monomer units in a chain or branch) of potato amylopectin found that the distribution of short chains ranges from a degree of polymerization (DP) of 6 to 35 or 36, with an average chain length of 14 – 17 residues, with the peak seen at DP 13 – 14 (Aberle, Burchard, Vorwerg, & Radosta, 1994); these chains are confined to a single crystalline lamella. Longer chains (DP > 37) cross more than one lamella, are mainly centred around DP 48–57, and consist of at least two subgroups with weight-average DP ~58 (B2 chains, crossing two lamellae) and 73 (B3 chains, crossing three lamellae) with a molar ratio of short to long chains of 5.3:6.5 (Noda et al., 2005). Long chains, with DP > 100, were also found in small amounts (Noda et al., 2005). These chain-length distributions have significant effect on properties such as crystallinity, gelatinization and viscosity, which in turn affect cooking and sensory (mouth-feel) properties.

Amylose is the smaller component of starch, varying from 15-35% (Tester & Morrison, 1990). It has a molecular weight of ~$10^{5–6}$ and is largely a linear polymer with a small number of randomly located long chains. These long branches however significantly affect many functional properties, e.g. hardness and stickiness in rice (Li, Prakash, Nicholson, Fitzgerald, & Gilbert, 2016). The amylose forms amorphous conformations, or single complexes with lipids, in the amorphous layers and among the amylopectin crystallites (Witt & Gilbert, 2014).

Potato starch has a lower gelatinization temperature compared to other starches. The low gelatinization of potato starch is considered to be partly due to the higher levels of phosphate monoester derivatives compared to starches found in grains, and the abundance of the B-type crystalline structures (Jane et al., 1999). The negative charges of the phosphates adjacent to the amylopectin chains repel each other, weakening the hydrogen bonds in the crystalline structure. These weakening bonds then allow water to readily destabilize the granular structure, reducing the gelatinization temperature (Jane et al., 1999). The B-type structure is characterized by a large proportion of long amylopectin branches (Gilbert, Besnard, Reeve, Lambides, & Hasjim, 2013) and fewer short branches (Hizukuri, Takeda, & Yasuda, 1981). This structure is formed by an open hexagonal packing of the double helices and contains 36 water molecules per unit cell (Takahashi, Kumano, & Nishikawa, 2004).

The rate and extent of gelatinization is affected by excess free water, temperature, exposure time (Spigno & De Faveri, 2004). Most of the potato starch in the french fry strip is fully gelatinized under excess water conditions during blanching. The decrease in crystallinity

depends on the water available to penetrate the starch granules and then to complete the melting process (Svensson & Eliasson, 1995). Most of the water inside the potato cell wall is contained within vacuoles, nucleus and cytoplasm (84%), the rest being in the starch granule (13%) and cell wall material (3%) (Rutledge, Rene, Hills, & Foucat, 1994). Starch requires 14 water molecules per glucose unit to be fully gelatinized (Donovan, 1979), independent of the granule size and degree of crystallinity (Wang, 1993). There are up to 3 to 4 layers of water immobilized by H bonding around the starch molecules that are gelatinized when excess water is available (Wang, 1993). However, starch granules in the middle layers may not be completely gelatinized, as they do not reach the right conditions (temperature, duration) due to the thickness of the potato fry. Consequently, gelatinization in the inner layers may only be completed during frying under constrained/reduced water conditions, as water is available for a few seconds before it evaporates. Potato chips, which are usually 49 mm in diameter and 20 mm long, have shown under the microscope to have two distinct layers of starch (external and internal) after gelatinization (Lamberg & Olsson, 1989). The external layer shows starch granules that are completely swollen and no detectable Maltese cross, while the internal layer contains raw starch granules that have clear Maltese crosses (Lamberg & Olsson, 1989). Under limited water , the majority of the starch is melted, not gelatinized (Donovan, 1979), since melting is independent of water content. Melting is a phase transition from crystalline to amorphous structure, and the energy required for the transition is supplied by heating the starch (Wang, Chiang, Zhao, Zheng, & Kim, 1991).

The gelatinization of potato starch is further affected by particle size; small granules require higher temperature (68 – 72^{o}C) to gelatinize compared to large granules that gelatinize at around 60 – 65^{o}C (Hasjim, Li, & Dhital, 2013). It is well established that potato starch granules not only vary greatly in size but also in their size distribution among potato tissues (Reeve, 1967). Small granules (<1 to 10 µm) are usually found in the vascular tissue, while larger granules are located mainly in the internal phloem. The pith area also contains large granules, but at lower abundance than in the internal phloem. Starch granules are very abundant in the cells between the vascular bundle ring and the skin.

Two blanching methods are widely used by the industry, with different effects on texture: high temperature and short time, and low temperature long time. High blanching temperatures (80–100^{o}C) destroy the catalytic activity of polyphenol oxidase (PPO) (Bingol, Wang, Zhang, Pan, & McHugh, 2014) and cause loss of firmness. PPO causes enzymatic browning through the oxidation of phenolic compounds into quinones (Jolivet, Arpin,

Wichers, & Pellon, 1998). Blanching at high temperature (80–100^{o}C) for 15 minutes causes the potato tissue to become softer with increasing blanching duration. Hydration, swelling and gelatinization of starch, together with β eliminative cleavage and pectin solubilisation, are mainly responsible for this tissue softening. Complete gelatinization of potato starch occurs from 65–75^{o}C, depending on moisture content and exposure time (Sablani, 2009) and for example is achieved at 67.5^{o}C in 2 minutes (Verlinden, Yuksel, Baheri, De Baerdemaeker, & Van Dijk, 2000). The pectic substances in the cell walls and middle lamella start solubilizing at ~60 ± 10^{o}C, causing a reduction in cell adhesion and increase in cell separation (Moyano, Troncoso, & Pedreschi, 2007).

Blanching at low temperatures (55–75^{o}C) causes leaching of sugars and reinforcement of the cell wall structure. The level of reducing sugars (fructose, glucose) in potatoes is critical in cooking, as sugars react with amino acids at high temperature (Maillard reaction) causing undesired colour formation during cooking. The firmer vegetable texture in potatoes has been extensively studied, and is the result of the activation of the pectin methyl esterase (PME) during low-temperature (50–70^{o}C) blanching (Andersson, Gekas, Lind, Oliveira, & Oste, 1994). Specifically, this firming effect is due to reduction in the level of methyl esterification of pectin in the middle lamella, which allows for more 'calcium bridging' between the free carboxylic acid groups (Tijskens, Waldron, Ng, Ingham, & Van Dijk, 1997), and less pectin chain cleavage by a β eliminative mechanism (Anthon & Barrett, 2006). Prolonged heat treatments can cause cleavage of the pectin chain next to a methyl esterified galacturonic acid residue; however, a reduced level of methyl esterification decreases the occurrence of pectin migrating through this cleavage (Anthon & Barrett, 2006). When potato tissue is heated to 50–70^{o}C, the PME interacts with the methyl ester groups and produces free carboxylic acid (Ni, Lin, & Barrett, 2005; Nourian & Ramaswamy, 2003; Andersson, Gekas, Lind, Oliveira, & Oste, 1994). At these temperatures, the cell wall is disrupted, leading to increased permeability. This increased permeability in turn allows migration of solutes from the cytoplasm and vacuole to the membrane, providing a high enough concentration of potassium (0.12 M) to activate pectin methyl esterase. Cation diffusion (Ca^{2+} and Mg^{2+}) establishes cross linking between chains, strengthening the tissue against thermal degradation. Heating temperature (60–70^{o}C) affects not only the rate at which starch gelatinizes but also the extent of calcium migration, because most of the calcium ions are bound to starch and can mobilize to the cell wall after starch is gelatinized (Van Dijk et al., 2002).

Cell-wall polymers determine the many of the characteristics of the plant and influence organoleptic characteristics such as texture (Taylor, McDougall, & Stewart, 2007). Parenchyma cell walls in potato obtain their strength from the cellulose microfibrils which are hydrogen-bonded to xyloglucan (Van Marle et al., 1997). This insoluble structure is embedded in a pectic polysaccharide matrix that acts as 'glue'. A strong cell wall gives turgor to the tissue as it limits expansion of the cytoplasm (Andersson, Gekas, Lind, Oliveira, & Oste, 1994). The interstitial layer between adjacent cell walls, in the middle lamella, contains high levels of pectin and acts as intercellular adhesive (Jarvis, Mackenzie, & Duncan, 1992). The middle lamella exerts a large influence on the way cells separate or rupture at the point of least resistance (Kaur & Singh, 2004). Cell separation occurs as a consequence of the reduction in intercellular adhesion between adjacent cells, due to thermal degradation of the pectic polysaccharides during cooking, which in turn increases intercellular distance in parenchymatous tissue. Calcium ions and pectin methyl esterase have the opposite effects to pectin on cell separation, because they link adjacent pectin molecules together. The firming effect of pectin crosslinking can be reduced by the capacity of phytic acid to bind Ca^{2+} and Mg^{2+} (Thybo & Martens, 2000).

Pre-drying

Pre-drying treatments reduce crust permeability (Lamberg & Olsson, 1989), moisture content and oil uptake after frying. Drying causes a 'skin' layer to form on the surface of potatoes, which helps to reduce vapour transport through the surface, as porosity is reduced. As porosity reduces, less void space is available for oil to remain after frying. Oil uptake usually occurs after frying, caused by condensation and capillarity forces.

Manufacturers aim to increase the dry matter of potatoes by pre-drying before frying, as the dry matter content of potatoes is a contributory factor to mealy texture in fries. Tubers with high dry matter produce chips that absorb less oil during frying (Lulai & Orr, 1979). Krokida et al., 2000 found that oil content in chips was reduced as drying time increased.

Blanching is performed before the drying process to avoid the development of colour and flavour defects that are caused by the PPO activity on polyphenols. Blanching also enhances drying rates as it causes the cellular network to loosen, reducing tissue cohesiveness (Fernando, Ahmad, & Othman, 2011).

Par Frying

Frying is a heat and mass transfer process which causes substantial chemical and organoleptic changes in the potato. Aguilera et al. (2001) used light microscopy in heat stage experiments to determine the changes starch granules undergo during frying. They heated a single potato cell in oil at a rate of 40^{o}C /min and observed that swelling of granules started at 72^{o}C and finished at 80^{o}C with minor deformation. They observed that water inside the cells is rapidly absorbed by starch granules before it evaporates. The granule expands and fills the entire cell, and loses birefringence without rupturing during gelatinization. Compaction of granules happens at 85^{o}C, and dehydration starts at around 100^{o}C, when water is released from the gelatinized starch. Distorted granules showed that most cells suffer dramatic changes but do not lose their integrity. These temperatures are higher than the gelatinization temperatures reported by other authors, as heating rates in these experiments were very high in order to simulate frying conditions. Frying experiments with isolated starch granules show that starch granules inside the cells swell later than the isolated starch granules (Bouchon & Aguilera, 2001).

Cell separation between adjacent cells happens as the water vapour generated during frying is quickly entrapped in the crust, and builds up pressure in the intracellular spaces. The super-heated steam leaves the product through intercellular passages, pulling cells apart (Moyano & Pedreschi, 2006). Weakening of the middle lamella also contributes significantly to cell separation, as the peptic material dissolves and the intercellular spaces are enlarged.

The crust develops when the surface temperature reaches ~103^{o}C (Costa, Oliveira, & Boutcheva, 2001). Crust is formed within seconds of frying, as the outer cells of the chips are damaged during cutting and undergo rapid release of vapour and subsequent dehydration. The crust becomes thicker as frying proceeds. Cells in the crust shrink and the cell walls become wrinkled around dehydrated starch. Cells in the crust look much smaller than those of fresh potato (Lisińska & Gołubowska, 2005), due to evaporation. Blister structures can form under the crust as vapour pressure is released, forming pockets. Blisters increase with temperature and cooking time (Costa, Oliveira, & Boutcheva, 2001).

Crust crispness is affected by surface porosity and roughness developed during frying as water evaporates. The level and intensity of evaporation will determine the porosity, density and volume of the fry (Pedreschi, Moyano, Santis, & Pedreschi, 2007). Intense and explosive evaporation will lead to large pore formation.

The level of crispness in french fries is affected by the amount of oil/fat in the crust surface (Van Vliet, Visser, & Luyten, 2007). Confocal microscopy shows that oil is located at the crust between the cell channels formed by the passage of steam during frying. Cell walls do not allow oil inside the cells, as they only contain dense starch in the interior. Oil is drawn to the intercellular space by suction as water vapour cools down after frying (Aguilera, Cadoche, López, & Gutierrez, 2001). The amount of oil present in chips is a balance between the amount of oil that is available (i.e. which adheres to the crust) and the porous space left by the water vapour (Bouchon & Aguilera, 2001). The amount of oil adhering to the crust is affected by the surface topography - potatoes with higher roughness tend to absorb more oil than smoother potatoes (Pedreschi, Aguilera, & Pyle, 2001).

Freezing

French fries are delivered frozen to consumers or retailers. Freezing is a way to preserve the product by reducing its water activity, microbial growth, and enzymatic activity (Shayanfar, Chauhan, Toepfl, & Heinz, 2013). It also maintains firmness, and organoleptic properties (Gonçalves, Pinheiro, Abreu, Brandão, & Silva, 2010).

The texture of a frozen product after subsequent cooking is largely affected by the size of ice crystals formed during freezing and their location inside the tissue. Most freezing technologies aim to avoid formation of large ice crystals inside the cells, by using a range of different freezing protocols (Ammar, Lanoisellé, Lebovka, van Hecke, & Vorobiev, 2010). The number and size of crystals formed during the crystallization process depends on the time spent in the critical temperature zone ($0 - 5^{o}C$) of ice nucleation and growth, and the amount of water available for freezing (Freschi, Doran, Malumba, & Blecker, 2014). For gelatinized starch-based gels, the crystallization process in the critical temperature zone also depends on the final properties of the heated starches and their water-binding capacity (Freschi, Doran, Malumba, & Blecker, 2014).

Effects of PEF

This review addresses what is currently known about the effects of PEF on the structural properties of potatoes (water release, mass transfer of small molecules and ions, enzyme

activity, oil content, cell wall structure, effects on pectin structure, etc.) that affect crispness and mealiness in french fries (Fig. 2). The scope of this review encompasses french fry processing and the response of the potato PEF-treated tissue to those treatments.

The potato tuber is made up of several layers with compositional differences in starch, pectin and amino acids, and different cell size and packing arrangements (Oey, Faridnia, Leong, Burritt, & Liu, 2016; Reeve, 1967). The cortex layer lies underneath the skin, and is a thin layer of parenchyma tissue that is rich in pectin and round and oval-shaped starch grains. The vascular storage parenchyma lies within the cortex shell and is rich in starch. The phloem and xylem are located within the boundary between the cortex and the vascular ring, with the water core, or medulla region, forming a central region with small cells and low starch content (Andersson, Gekas, Lind, Oliveira, & Oste, 1994). Potato tissues exhibit different electric conductivity and hence a heterogeneous distribution of damaged electroporated cells along the tuber, due to differences in tissue structure and composition. Studies on the effect of PEF on potato microstructure and distribution of electroporation along the tuber confirm the heterogeneous tissue response to PEF treatment (Oey, Faridnia, Leong, Burritt, & Liu, 2016). Magnetic resonance electrical impedance tomography studies on PEF potatoes showed an asymmetric electric field distribution along potato tissues, with the electric field intensity value being highest on the region closest to the electrodes and lowest on the tissues most distant from the electrode (Kranjc, Bajd, Serša, de Boevere, & Miklavčič, 2016). Enzymatic browning from polyphenol oxidase activity on the PEF treated tissues was used to visualize the effect of PEF along potato tubers. PEF electrode probes were inserted in the potato and the cell damage was visualized by the intensity of the browning, which was found to be not uniformly distributed, with the water core region being the darkest (Castellví, Banús, & Ivorra, 2015). Cell viability was measured on peeled and unpeeled potatoes using a tetrazolium salt staining, which showed uneven distribution of dead cells along the multilayers of potato tissues. The inner medulla, water core and vascular ring were the tissue most affected by the PEF treatment and the outer medulla the least affected (Faridnia, Burritt, Bremer, & Oey, 2015).

Water transfer

PEF increases membrane permeability causing cells to release water - the higher the field strength, the greater the amount of water lost (Weaver & Chizmadzhev, 1996). Water can

migrate in a tissue by transmembrane transport via tonoplast and plasmalema and by symplastic transport through the cytoplasm and the apoplastic cell wall (Tyree, 1970). PEF treatment seems to cause permeabilization not only of the cell membrane but also the vacuolar membrane (Fincan & Dejmek, 2002). Water mobility was measured in PEF treated carrot tissue using H nuclear magnetic resonance (Aguiló-Aguayo et al., 2014). The PEF treated carrot samples exhibited overlapping peaks that were well defined in the untreated samples, indicating greater water diffusion due to increased membrane permeability and/or loss of integrity of the barrier between vacuole and cytoplasm. The PEF treated cells showed the vacuole content mixed with the extracellular liquid, indicating that water in the PEF treated cell moved from vacuoles to cytoplasm to outside the cell. Changes in the intracellular region are followed by the changes in the extracellular region, as a voltage gradient in the cytoplasm cannot develop in an intact plasmalemma. PEF-treated carrot tissues also showed a significant decrease in the relative area of the NMR relaxation peak related to cell walls, indicating that bound water in cell walls decreased in the PEF-treated tissue (Aguiló-Aguayo et al., 2014).

Increased membrane permeability would be desirable during french fry manufacturing, as water release is one of the targets of processing. Water reduction increases the percent of dry matter and it is well known that potatoes with high dry matter produce french fries that are mealy (Donovan, 1979). Water content decreases gradually during processing, starting at around 80% in raw potatoes and finishing at 45-50% after pre-drying and frying (Lisińska & Gołubowska, 2005). Pre-drying is conducted to reduce water content and to form a skin layer to reduce crust permeability. During frying, not only the initial water content but water-vapour behaviour is relevant to the final texture. Permeable cells (PEF treated) tend to release water much more easily by forming a water vapour layer which provides a barrier against oil penetration.

Following PEF treatment, a reduction in drying time, temperature, and an increase in water lost during pre-drying of PEF raw potato slices have all been observed. PEF treatment (electric field E = 400 V cm^{-1}) of potato tissues enhances convective drying and allows a decrease in drying temperature of around 20^{o}C (Lebovka, Shynkaryk, & Vorobiev, 2007). Reduction in drying times of up to 1/3 have been reported for potatoes that had undergone PEF treatment (Knorr & Angersbach, 1998). PEF-treated potatoes lost 4% more water than

the untreated potato after 10 min in a drying oven at 100°C. A water reduction of around 8% was achieved after another 20 min at 200°C (Janositz, Noack, & Knorr, 2011).

Reductions in drying rates due to PEF have also been reported in other plant tissues. PEF-treated bell peppers exhibited a moisture content of 11% after only 3 h drying, compared to the untreated one with 16% after 5 h. A reduction of 25% in drying time was reported for PEF-treated paprika (Ade-Omowaye, Angersbach, Taiwo, & Knorr, 2001).

Experiments show that there is a clear effect of PEF in enhancing drying rate and lowering drying temperature in potatoes. However, all these experiments were conducted in raw tissue, where water transfer occurs without any interference from gelatinized starch. Gelatinized starch reduces the amount of water available inside the cell. Water inside the potato cell wall is mainly located in vacuoles, nucleus and cytoplasm (84%), and some (13%) in the starch granule (Rutledge, Rene, Hills, & Foucat, 1994). Real-time microscopy experiments showed that starch rapidly absorbed the water inside the cells when undergoing gelatinization (Aguilera, Cadoche, López, & Gutierrez, 2001). Gelatinized starch can act as a barrier for water flow, as starch undergoing gelatinization expands and fills the entire cell (Aguilera, Cadoche, López, & Gutierrez, 2001).

Oil uptake

PEF treatment in potatoes was found to be more effective than a blanching-induced gelatinized layer in reducing oil uptake in french fries. A reduction in oil uptake of 38.7% was obtained in the chips that were PEF treated and only 3.8% reduction was achieved in blanching treated samples (Janositz, Noack, & Knorr, 2011). During frying, water vapour forms a barrier for oil penetration (Van Loon et al., 2007) and PEF decreases oil uptake by facilitating water diffusion from the core of the potato strips to the surface, creating a thicker water vapour layer that leads to reducing dehydration and oil uptake. Reduction in oil uptake in the PEF treated potatoes can also be explained by the smoother surface of the PEF treated tissue leading to a better oil drainage after frying (Thanatuksorn, Pradistsuwana, Jantawat, & Suzuki, 2005).

The above studies were performed on raw potatoes where starch gelatinization had not occurred, so the effect of gelatinized starch on mass transfer has not been taken into account. Gelatinized starch can alter mass transfer—water evaporation—during frying.

Mass transfer during heating in oil may also be altered by the formation of ice crystals outside the PEF treated potato. French fries are usually sold frozen and most customers fry them straight from the packet. PEF-treated samples show evidence of ice crystal formation outside the cells (Jalté, Lanoisellé, Lebovka, & Vorobiev, 2009). Scanning electron micrographs of freeze-thawed potato showed deformation of the cells in both untreated and PEF treated potatoes. However, the damage and deformation on the cells that have been treated is larger than in the untreated ones. Studies on the effect of PEF on the rate of freezing on potato tissue showed that PEF-treated samples and PEF-untreated samples exhibited a very similar ice crystallization zone, and that they started freezing at the same time at –1˚C; however the PEF-treated sample freezes at faster rate than untreated potatoes, reducing freezing time (Jalté, Lanoisellé, Lebovka, & Vorobiev, 2009) .

Diffusion of low molecules and ions

Mass transfer in a cell is mainly regulated by the intact cytoplasm membrane that acts as a semipermeable barrier to migration of molecules (Puértolas, Luengo, Álvarez, & Raso, 2012). The enhanced permeability of the PEF treated membrane leads to a reduction in the resistance to mass transfer in cells. PEF treatment has been shown to enhance diffusion of low molecular weight compounds such as the reducing sugars fructose, glucose and sucrose. A PEF treatment (E = 1.5 kV cm^{-1} with 20 pulses) caused 30% reduction on fructose content on potatoes (Janositz, Noack, & Knorr, 2011). The release of reducing sugars contributes to a significant reduction in acrylamide in french fries. The Maillard reaction is responsible for the formation of acrylamide during frying as potatoes develop their brown colour, as asparagine or methionine react with the reducing sugars (fructose and glucose) at temperatures higher than 120^{o}C (Gökmen, Şenyuva, Acar, & Sarıoğlu, 2005). Acrylamide formation is a big concern, because this substance is known to cause cancer in rats (Pedreschi, Aguilera, & Pyle, 2001). Potatoes are one of the food product containing the highest amount of acrylamide. Similar results were seen on PEF treated carrots (E = 1 kV cm^{-1}): the extractability of sugars increased by 43% for sucrose and 48% for β-glucose compared to untreated tissue (Hossain, Aguiló-Aguayo, Lyng, Brunton, & Rai, 2015).

The effect of PEF on the kinetics of ion leakage (K^{+} and Ca^{2+}) has been studied using potato cubes (Faridnia, Burritt, Bremer, & Oey, 2015). It was observed that the medium conductivity increased as PEF intensity and duration increased. Potassium leakage was

highest, followed by that of calcium. The level of released K^+ increased as the intensity of the treatment increased; however, this was not the case for Ca^{2+} release.

Starch properties

The effect of PEF on the potato starch physico-chemical properties has been studied on commercial starch slurries and in raw potatoes. However these results are conflicting. PEF treated commercial starch show changes in starch surface and in the particle size distribution, while the effect of PEF was not noticeable on the treated raw starch. Cryo-scanning electron microscopy studies of PEF treated starch granules on raw potato showed no changes in the shape or size of the granule (Faridnia, Burritt, Bremer, & Oey, 2015). In this study, raw potatoes received electric field strengths between 0.2 and 1 kV cm^{-1}.

A 8% slurry solution of commercial potato starch with KCl was subjected to strong PEF treatments (30, 40, 50 kV cm^{-1}) (Han et al., 2012). Samples did not exceed temperatures higher than 50^{o}C. Scanning electron microscopy and laser scattering measurements showed changes in the starch surface and particle size distribution in the PEF treated starch samples. The surface of the treated starch looked rough and damaged, with some granules aggregating, while the untreated starch had a smooth surface. The particle size distribution of the starch granules changed in the PEF treated sample, with an increase in the number of larger granules. PEF-treated starch granules were able to grow in size and to aggregate as their outer parts were damaged and able to absorb more water. The X-ray diffraction pattern of treated starch showed some reduction of crystallinity, that of the native starch being 27.3%. With a PEF treatment of 40 kV cm^{-1}, the relative crystallinity of the starch decreased to 6.2 %, and at 50 kV cm^{-1}, it was further reduced to 3.3%. These results indicate that starch crystallinity is reduced by PEF treatment, whence the starch granule can react with water molecules more easily. Further evidence of effect of PEF on starch crystallinity was observed as starch enthalpy decreased in the PEF-treated samples. Starch pasting properties as measured in the Brabender Viscograph were also affected by the PEF treatment. The peak and breakdown viscosity decreased as the PEF treatment increased.

The effect of PEF varies between the purified commercial starch slurry and native starch granule. PEF treatment is applied to the raw potato during french fry production. Therefore, we cannot conclude from the above experiments anything about the effect of PEF on the starch granule at the tuber level and its effect on french fry texture.

Enzyme activity

It is reasonable to expect enzymes to be affected by electroporation caused by PEF: enzymes are proteins and protein higher-level structures involve electrostatic interactions. The degree of denaturation with PEF depends on the enzyme, temperature, electric field intensity, pulse width, number of pulses, pulse waveform, field polarity and medium (Giner, Gimeno, Barbosa-Cánovas, & Martín, 2001). Polyphenol oxidase (PPO) and pectin methyl esterase (PME) are probably the most relevant enzymes impacting potato processing. PPO produces brown pigments, namely quinones, from the oxidation of polyphenols, giving an undesirable effect on the flavour and colour of the potato tissue. Activation of PME has a firming effect on potatoes which is due to reduction in the level of methyl esterification of pectin in the middle lamella, which allows for more 'calcium bridging' between the free carboxylic acid groups (Tijskens, Waldron, Ng, Ingham, & Van Dijk, 1997). There have been several studies on the effect of PEF on those enzymes, but the various results are difficult to compare and it is hard to develop a clear understanding of the effect of PEF on those enzymes and extrapolate that to the quality of french fries. Firstly, some of these experiments lack temperature control and equipment standardization. Therefore, it is difficult to establish if enzyme denaturation was partly caused by the rise in temperature or by treatment intensity. Furthermore, most studies in PPO and PME have been conducted on mushrooms (Ho, Mittal, & Cross, 1997), pears, peaches, and apples (Giner, Gimeno, Barbosa-Cánovas, & Martín, 2001; Van Loey, Verachtert, & Hendrickx, 2001) and very few on potatoes. The composition of the matrix is very important because it influences PEF treatment and enzyme behaviour. Lastly, enzyme inactivation levels reported are quite broad: some researchers reported levels of PPO inactivation of up to 97% (Giner, Gimeno, Barbosa-Cánovas, & Martín, 2001), others found 30% and 40 % maximum level of inactivation in buffer solutions at pH 6.5 (Van Loey, Verachtert, & Hendrickx, 2001; Ho, Mittal, & Cross, 1997). Experiments conducted on the PPO of pears and apples reported a residual activity (RA) for apple PPO of 3% at 24 kV cm^{-1}, and for pear PPO of 38% at 22.3 kV cm^{-1} under the same treatment duration of 6 ms (Giner, Gimeno, Barbosa-Cánovas, & Martín, 2001). Temperatures during the experiment were not reported but it was stated that temperatures did not rise above 25^{o}C, and samples were cooled in a cold water bath at regular intervals. Other researchers measured PPO enzyme activity in two very different sets of samples, one with PPO in apple juice, and the other with PPO in buffer solution with the same pH and electrical conductivity as in the

freshly squeezed juice (Van Loey, Verachtert, & Hendrickx, 2001). The PPO activity in the buffer solution was reduced to around 30% after PEF treatment with a pulse frequency up to 10 Hz, 1000 pulses of 40 s at 7 kV cm^{-1}. This treatment increased temperature to 60^{o}C, and the level of inactivation is almost certainly partly related to the temperature change. Lower PEF treatment did not cause an increase in temperature, nor did it achieve any reduction in enzyme activity. However, PEF treatment of freshly squeezed apple juice increased PPO activity. Levels of 30–40% reduction in activity were reported on purified commercial enzymes when 24 kV and 30 pulses were applied (0.3 electrode distance, 2-s pulse period) (Ho, Mittal, & Cross, 1997).

There are considerable discrepancies between the various PME inactivation levels reported under PEF treatments. While some researchers found a high level of inactivation (88%) on orange juice with E = 35 kV cm^{-1} for 5 µs (Yeom, Streaker, Zhang, & Min, 2000) and 93.8% on tomato at 24 kV cm^{-1} (Giner et al., 2002), others found very low levels of inactivation of 10% (1000 pulses of 1 µs at 1 or 2 Hz and field strength up to 35 kV cm^{-1}) on PME extracted from fresh juice and dissolved in buffer solution; even an increase level of PME was found in the freshly squeezed juice (Van Loey, Verachtert, & Hendrickx, 2001).

There is a lack of research on the effect of PEF on the mechanism of enzyme inactivation and on enzyme-substrate availability after treatment. Enzymes in general tend to be more resistant to PEF than microorganisms (Ho, Mittal, & Cross, 1997; Vega-Mercado et al., 1997) and require stronger electrical conditions before denaturing occurs (Giner, Gimeno, Barbosa-Cánovas, & Martín, 2001). Electrical pulses can affect the three-dimensional structure of an enzyme, as these are governed by weak non-covalent forces, hydrogen bonds and hydrophobic interactions (Ohshima, Tamura, & Sato, 2007). PPO activity may increase after PEF treatment. PPO is found in the plastids or chloroplast and polyphenol compounds are secondary metabolites found in vacuoles (Arevalo, Ngadi, Bazhal, & Raghavan, 2004). The plasmalemma and tonoplast both become more permeable due to the PEF treatment, and decompartmentalization of substrate and enzyme can result in them mixing; in the presence of oxygen, PPO would oxidize the phenolic compounds producing undesirable coloured compounds (quinones). Enzymatic browning due to PPO activity has detrimental effects on the sensory and nutritional characteristics of french fries (Queiroz, Mendes Lopes, Fialho, & Valente-Mesquita, 2008). Enzymatic browning can occur during manufacturing of french fries after potatoes are PEF treated and before they are cut, blanched and dipped into a chelating solution.

Cell structure

There is little information on the effect of PEF on plant cell structure, architecture and composition of potatoes. Moreover, there are several inconclusive factors due to lack of agreement between different studies for some traits. Plant cell wall structure is comprised of primary and secondary cell walls that give higher rigidity to the cell (Bazhal, Lebovka, & Vorobiev, 2003). Some researchers found that electroporation produced a decreased in vacuole size and gaping (Fincan & Dejmek, 2002). A small increase in cell separation was seen on PEF treated potato tissue (E = 5 kV cm^{-1}, n = 20) stained with ruthenium red (Janositz et al., 2011). A quantitative measurement of lignin on PEF-treated asparagus showed a decrease close to 20% (Janositz, Semrau, & Knorr, 2011). SEM micrographs of potato tissues that went through a 400 V cm^{-1} field showed disintegration of potato issue of 0.95, but showed no visible changes in the starch surface or shape of the cells (Ammar, Lanoisellé, Lebovka, van Hecke, & Vorobiev, 2010).

Conclusions

There is a wealth of information on the technical conditions of PEF treatment that cause cell death. Research is needed to determine the electric field distribution on the heterogeneous layers of potato tissues caused by the PEF treatment and the effect on the structural properties that affect french fry texture. Moreover, most of the research conducted on the effect of PEF on water transfer, oil uptake, diffusion of small molecules and ion content in potatoes has been conducted on raw tissue. Therefore, conclusions cannot be drawn on the effect of PEF on the final texture of french fries, which is the result of the effect of the process steps (steam peeling, PEF treatment, pre-drying, blanching, par frying, freezing and drying) and their interactions on the tuber structural properties.

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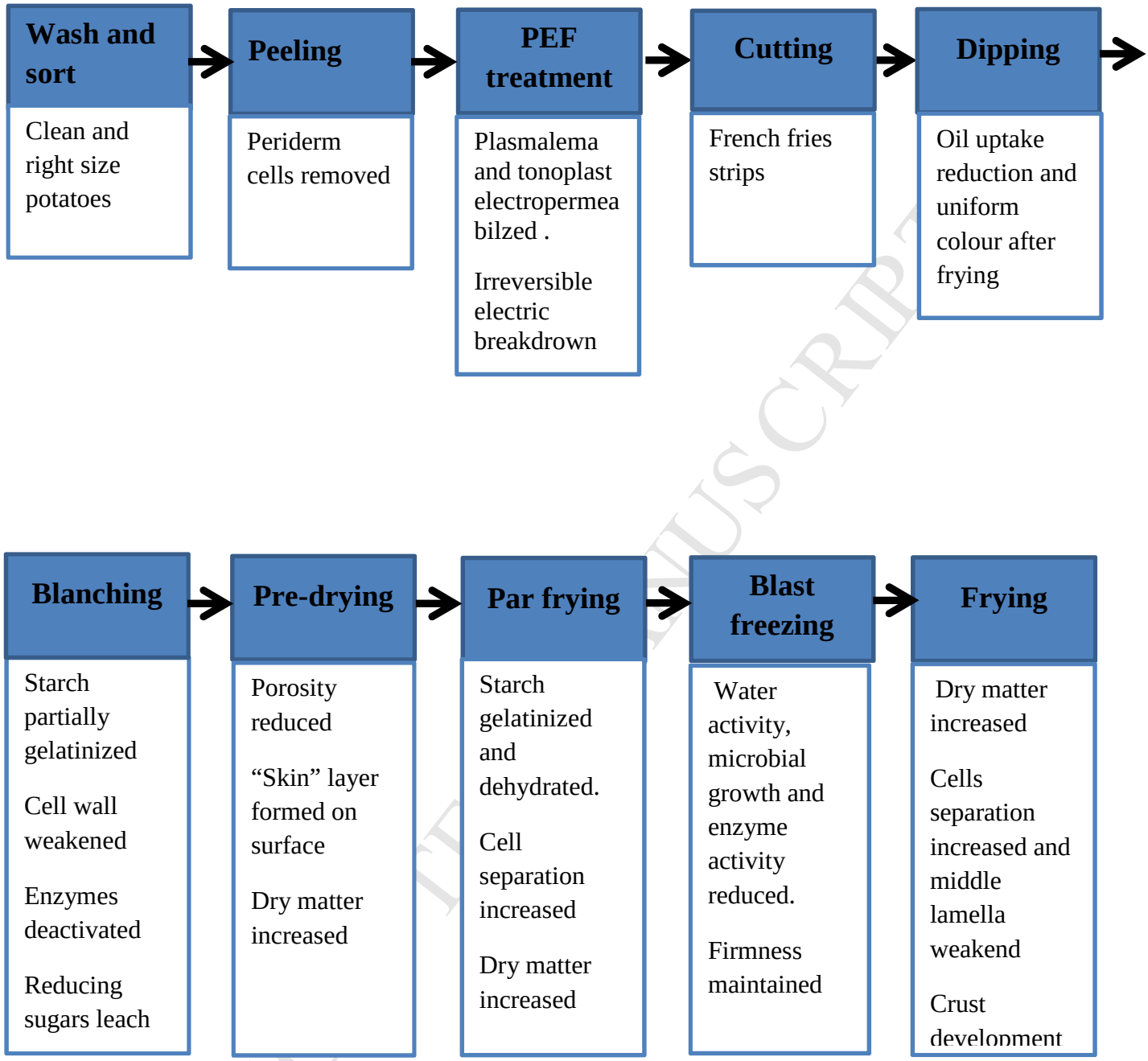

Fig.1 French fry manufacturing process

*PEF treatment can be performed before or after peeling

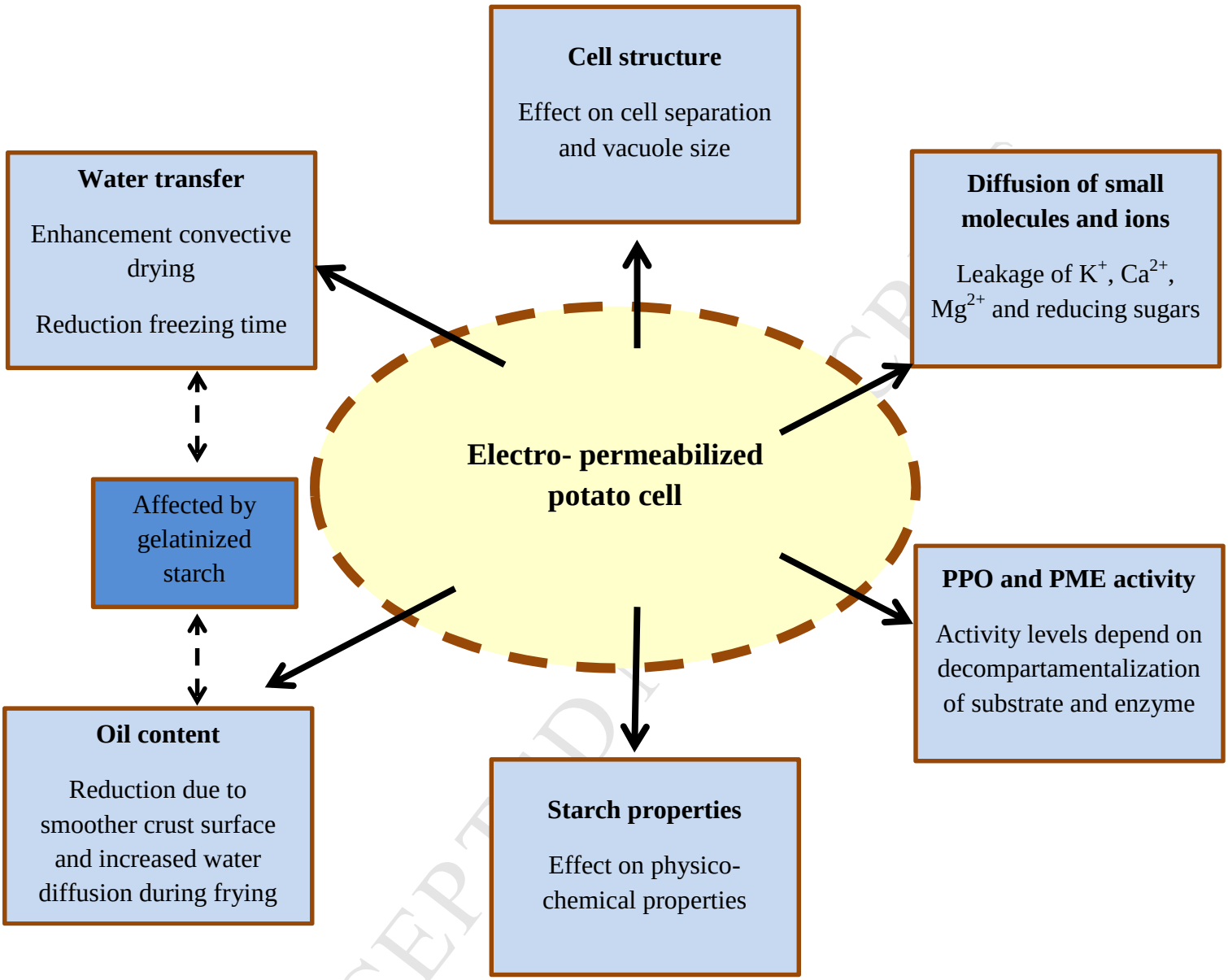

Fig. 2 Effect of PEF on the structural properties of potatoes that affect french fry texture

Highlights

This review outlines the current research on the effect of PEF on the structural properties that affect French fry texture. It also discusses the shortcomings of the research in relation to the french fry manufacturing process.