Chapter 3
Engineering and Nonthermal Technologies: Process Optimization Through Kinetic Modelling

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1 Introduction

Food research and innovation during the last 50 years has significantly offered in the technological advancement. Significant effort has been targeted on the production of safer, of higher quality, of improved nutritional profile foods, as well as in the development of new-novel food products that could not be produced, or their safety and stability could not be ensured by the conventional equipment and knowledge. Novel Nonthermal technologies in food processing are among the technology advancements. Their aim is mainly to substitute conventional thermal treatment applied for the pasteurization and sterilization of foods, while simultaneously retaining their quality and nutritional characteristics. High pressure (HP), Pulsed Electric fields (PEF), Pulsed Electromagnetic Fields (PEMF), Cold Atmospheric Plasma (CAP) and Osmotic Dehydration (OD) are the most important novel technologies studied and (some of them) efficiently applied in an industrial environment.

Although the research activity on novel Nonthermal technologies has been continuously growing the last decades (Fig. 3.1) resulting in production of data, thus continuously growing application of some of the novel technologies, some scientific, technological, and technical issues should be answered. Food industry demands fully documented and validated answers with regards to the applicability and the benefits of all these technologies, as physical processes of food preservation. Process optimization (selection of most appropriate process conditions) for the production of safer, high quality, nutritious, cost effective and consumer acceptable products is essential. The implementation of the scientific achievements for an effective process is based on the kinetic approach of the destructive reactions of several factors that

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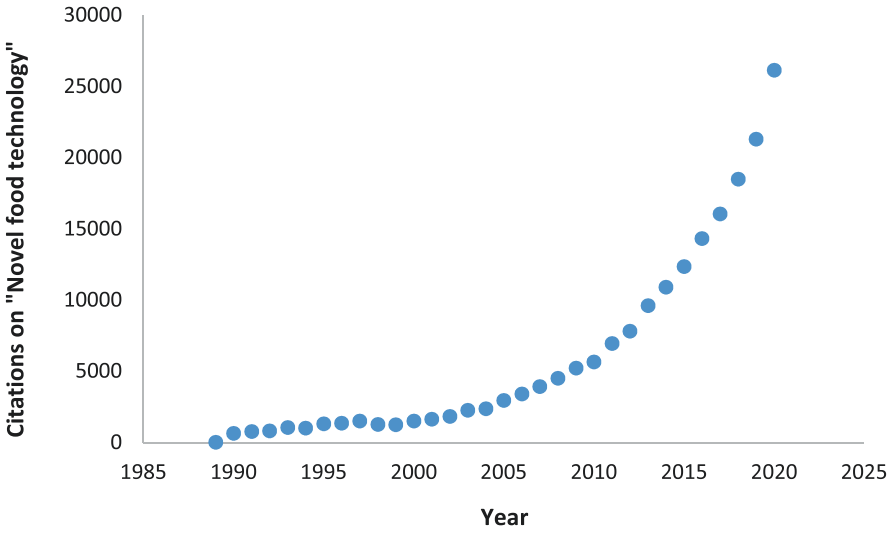

Fig. 3.1 Number of cited papers in the literature through years (keywords: novel and food and technology)

lead to spoilage or degradation of food, during the novel technologies' treatments. A systematic study of the technical parameters would allow for food engineers to predict and evaluate for the process applied, its intensity and efficiency, enabling the use of corrective actions if needed, for production of safe, sustainable, and cost-efficient final food products.

Although the novel technologies are aimed to substitute conventional thermal treatment, there is still research being conducted even for the well-studied thermal processing that has only two process parameters (temperature and time). For all the other Nonthermal technologies, that the number of their variables is higher (Table 3.1), it is evident that for the production of data, increased number of experiments has to be conducted.

Depending on the product to be treated, the dependent variables need to be named and studied as a function of the independent variables of each technology applied. The most important quality and safety parameters to be studied are the pathogens inactivation, the spoilage microflora inactivation, the endogenous deteriorative enzymes inactivation and the non-alteration of colour, texture, pH value, nutritional characteristics and finally organoleptic acceptability. The mathematical description of the effect of independent variables (process parameters) on the safety and quality indices of the treated foods is of high importance since allows for the food engineer to optimize the process; mathematical equations describe the effect of the process parameters values on selected quality indices. Thus, food engineers save time and money by not applying the trial and error approach for the selection of the appropriate conditions for the Nonthermal treatment.

Table 3.1 Number of independent variables for each process nonthermal technology

Technology	Number of variables	Independent variables
High pressure	3	P: Pressure T: Temperature t: Treatment time
Pulsed electric fields	7	E: Electric field strength t: Treatment time s: Shape of pulse w: Width of pulse f: Frequency Q: Specific energy T: Temperature
Pulsed electromagnetic fields	7	M: Magnetic field strength t: Treatment time s: Shape of pulse w: Width of pulse f: Frequency Q: Specific energy T: Temperature
Cold atmospheric plasma	9	F: Flow of the gas T: Temperature t: Treatment time l: Gap distance between electrode and food vol: Volume of food V: Voltage s: Shape of pulse w: Width of pulse f: Frequency
Osmotic dehydration	6	t: Treatment time T: Temperature $m_{solution}/m_{product}$: Solution-to-product mass ratio Type of osmotic solutes %C: Concentration of the osmotic solution Type and level of agitation

For all thermal and Nonthermal technologies, the mathematical description of the effect of process time on any food quality index is characterized as primary modelling. Within this approach, all other independent variables of each technology are kept constant, thus the effect on any chemical change, microbial population or enzyme activity is described by zero order, first order, second order or n^{th} order kinetics (Table 3.2) (Labuza 1984; Saguy and Karel 1980). First-order kinetics is the one mostly applied in nonthermal processing for the estimation of the rate constant of a quality index alteration vs process time and will further be discussed within this chapter.

The primary models are useful when the processing conditions (values of the independent variables for each Nonthermal technology) are kept constant. For processing conditions that are changed, new experiments should be performed to

Table 3.2 Reaction order kinetics applied for the mathematical description of the effect of process time on any microbial, enzymatic or chemical index

	Zero order	First order	Second order	nth order
Rate law	$-d[C]/dt = k$	$-d[C]/dt = k[C]$	$-d[C]/dt = k[C]^2$	$-d[C]/dt = k[C]^n$
Integrated rate law	$[C] = [C]_0 - kt$	$[C] = [C]_0 e^{-kt}$	$1/[C] = 1/[C]_0 + kt$	$[C]^{n-1} = [C]_0^{n-1} - (n-1)kt$

estimate the corresponding new primary model parameters. For a number of different process conditions studied with simultaneous application of primary models for each alteration of the process conditions, new mathematical equations known as secondary models can be applied to express the independent variables parameters effect on the predicted primary model parameters. These equations are the result of theoretical considerations or empirical observations and in most cases are nonlinear.

2 High Pressure Processing

The initial interest of the scientific community in the application of High pressure (HP) technology included inactivation of microorganisms such as bacterial stem cells, yeasts and fungi (Hoover et al. 1989; Patterson et al. 1997; Smelt 1998). The main target was, through HP processing optimization, to increase foods shelf-life by inactivating spoilage and pathogenic bacteria (Bayindirli et al. 2006; Donaghy et al. 2007; Jofré et al. 2008). HP causes microorganisms cellular membrane damage and is mainly reported for pathogenic and spoilage bacteria vegetative forms when food is treated with pressures higher than 200 MPa, where irreversible protein/enzyme denaturation and intracellular content leakage occur. The effects of HP on enzymes (mainly pectin methylesterase, polyphenoloxidase and peroxidases) has also been reported in a large number of studies cited in the literature (Irwe and Olsson 1994; Seyderhelm et al. 1996; Butz et al. 1996; Weemaes et al. 1997; Ludikhuyze et al. 1996, 1998, 2000; Indrawati et al. 2000; Nienaber and Shellhammer 2001; Moatsou et al. 2008a, b; Eylen et al. 2008; Katsaros et al. 2006, 2017; Boulekou et al. 2010). The conclusion of the studies is that HP significantly affects enzymes and enzymatic reactions, allowing for the development of an alternative to thermal treatment preservation technique that leads to reduced undesirable changes in the texture and sensory characteristics of a food product. The enzyme inactivation is mainly attributed to changes in the secondary and tertiary structure of enzymes occurring at specific pressures (Giannoglou et al. 2016). HP process of pressurization is based on the principle of "Le Chatelier," inducing a reduction in molecular volume and, consequently exponentially accelerating the occurrence of reactions favoured by pressure. Thus, the rates of the chemical or physical reactions resulting in lower volume products are accelerated by HP, whereas the reactions that result in an increase in the total volume are retarded. Based on the literature, the results show that different microorganisms and enzymes, exhibit different kinetic inactivation or activation with HP.

The observation from the researchers that the effect of HP processing, on a particular characteristic, over time follows a specific trend that could be kinetically expressed through mathematical modelling, led to the need mathematical models to be developed in order to predict the impact of HP processing on a specific characteristic (e.g., activity of enzymes, microorganisms etc). A mathematical model predicting the change of a target parameter as a function of time (primary model) is an essential tool when designing HP experiments and industrial processes. Furthermore, the application of a primary model can be extended if a secondary model describing the pressure dependence of the primary model parameters is available too. Below the most used primary and secondary mathematical models by various researchers in the field of HP processing are presented, to describe and predict the effect of HP on different microorganisms, enzymes and quality indices of various food systems.

2.1 Primary Mathematical Modeling

The main equations reported in the literature describing the effect of treatment time at constant pressure and temperature on the microbial, enzyme or any other quality index alteration are depicted in Table 3.3.

In Table 3.4, the effect of processing conditions range on the inactivation of indicative microorganisms and enzymes from various food products is depicted. The model used along with the model parameters estimated are also presented.

2.2 Secondary Mathematical Modeling

The primary models are useful when the processing conditions (pressure, temperature, pH, etc.) are kept constant. If any processing condition is changed, a new set of experiments must be performed to obtain new primary model parameters. To extend the application of primary models, mathematical expressions known as secondary models can be developed to estimate the pressure and/or temperature effect on the predicted primary model parameters. As in the case of primary models, secondary models can be obtained from theoretical considerations or empirical observations. Most of the secondary models here presented (Table 3.5) are nonlinear, reflecting complex biological behaviors under high-pressure/high-temperature conditions.

In most references cited in the literature, the Bigelow model is used to describe the effect of temperature and pressure on the reduction of microbial load. As in the case of thermal treatment, the thermal resistance constant z_T was developed is used, the analogous approach was established for pressure effect as well, estimating the pressure resistance constant z_P. Both these values may be used for the description of the effect of pressure (z_P) and temperature (z_T) on the decimal reduction time of microorganisms. The parameter z_P determines the pressure increase required to

Table 3.3 Mathematical equations cited in the literature and used for the description of the effect of treatment time at any combination of pressure and temperature on the value of microbial, enzymatic or chemical reactions

Model used	Observations
First order kinetics	
$\log_{10}(N/N_0) = -k \cdot t$ $\ln_{10}(N/N_0) = -(2.303/D) \cdot t$	A change in the initial concentration of an index, N_0 at t = 0, up to a value of the concentration equal to N after a process time, t, is described by an inactivation rate constant (k min^{-1}) under constant isobaric and isothermal conditions. Decimal reduction time, D (min) can be used for the microbial load reduction.
Fractional conversion model	
$C = C_\infty + (C_0 - C_\infty) \cdot \exp(-k \cdot t)$	Applied when part of a baroresistant or thermoresistant enzyme or isoenzyme or microbial load or component concentration with much higher resistance, C_∞ (t = ∞).
Multi phasic model	
$C = C_L \cdot \exp(-k_L \cdot t) + C_S \cdot \exp(-k_S \cdot t)$	The simplest form of the multiphasic model considers the presence of a labile fraction (C_L) that is inactivated more rapidly and a stable fraction (C_S) able to withstand longer treatment times. Each fraction is inactivated at a distinct rate, and the concentration (C) observed represents the sum of C_L and C_S at any given time
Weibull model	
$\log_{10}(N/N_0) = -b\ t^n$	The residual microbial/enzyme activity curve can be interpreted as a cumulative function of the distribution that dictates the treatment time at which the microorganism or enzyme will fail to resist and result in inactivation. The Weibull frequency distribution is applied, where N_0, the initial number of cells (CFU ml^{-1} or g^{-1}); N, the number of survivals after an exposure time t (CFU ml^{-1} or g^{-1}); t, the holding time (min) at pressure and b, n are the scale and shape factors respectively.

(continued)

Table 3.3 (continued)

Model used	Observations
Weibull biphasic model	
$N_{(t)} = N_0\left[f \cdot 10^{-(t/b'1)n_1} + (1-f)\cdot 10^{-(t/b'2)n_2}\right]$	When two bacterial subpopulations are present, the Weibull model is reparametrized as a function of the labile population fraction (f)
Log-logistic model	
$\log_{10}N = \alpha + (\omega - \alpha)/1 + \exp[4\cdot\Omega\omega - \alpha(\tau - \log_{10}t)]$	The maximum inactivation rate (Ω), and the time at which Ω occurs (τ), along with the dependent variable microbial population logarithm ($y = \log_{10}N$) and the independent variable logarithm of time ($\log_{10}$ t) were incorporated into the Log-logistic equation. Parameter ω was defined as the difference between the lower and upper asymptotes ($\omega = \beta - \alpha$)
Modified Gompertz model	
$\text{Log}_{10}N/N_0 = A\ \exp\cdot[-\exp\ [(\mu_{max}\ \exp(1)/A)\cdot\ (\lambda - t) + 1]]$	Parameter A represents the difference between the lower and upper asymptotes of microbial survival curves ($\log_{10}N/N_0$ vs time), μ_{max} is the maximum inactivation rate, and parameter λ is the inflection point, or the time at which the linear portion of the curve starts
Baranyi-Roberts model	
$y(t) = \ln x(t) = y_0 + \mu_{max}A(t) - \ln(1 + e\mu_{max}A(t) - 1*e(y_{max} - y_0))$	The model encompasses both the lag to exponential and exponential to stationary transitions of bacterial growth. Letting the bacterial concentration at time t be given by x(t), where, $y_0 = \ln x_{(0)}$, $y_{max} = \ln x_{max}$ are the initial and maximum bacterial concentrations respectively, μ_{max} denotes the maximum specific growth rate.

Table 3.4 Effect of High pressure processing conditions range on the inactivation of indicative microorganisms, enzymes and substituents from various food products as cited in the literature

Microorganisms	Environment	Processing conditions	Kinetic model	References
Aerobic bacteria	Fresh, whole, raw milk pH = 6.64	300, 400, 600 MPa 100–200 MPa s^{-1} 0–105 min 25 °C	First-order	Dogan and Erkmen (2004)
	Fresh, filtered orange juice pH = 3.35			
	Fresh, filtered peach juice pH = 5.21			
Aerobic bacterial spores *B. amyloliquefaciens* TMW 2.479 Fad 82 *B. amyloliquefaciens* TMW 2.482 Fad 11/2 *B. sphaericus* NZ14 *B. amyloliquefaciens* ATCC 49763 Anaerobic bacterial spores *C. sporogenes* ATCC 7955 *C. tyrobutylicum* ATCC 27384 *T. thermosaccharolyticum* ATCC 27384	Deionized water	700 MPa 0–5 min 105, 121 °C	First-order	Ahn et al. (2007)
Bacillus stearothermophilus spores	Egg	400, 600, 700 MPa 0–16 min 105.8 ± 0.6 °C	First-order	Rajan et al. (2006)
Lactobacillus delbrueckii subsp. bulgaricus ACA-DC0105	Phosphate buffer 20 mM pH 7.0	100–700 MPa 20–40 °C	First-order	Katsaros et al. (2009a)
Lactobacillus delbrueckii subsp. bulgaricus ACA-DC0105 *Streptococcus thermophilus ACA-DC0022* *Lc. lactis ACA-DC 0049*	Reconstituted skimmed milk	100, 200, 450 MPa 0–40 min 20, 30, 40 °C	Baranyi model	Giannoglou et al. (2019)
Pediococcus spp.	Raw seabream (*Sparus aurata*) extract	150–600 MPa 20–40 °C	First-order	Tsironi et al. (2015)
Escherichia coli	Fresh extracted carrot juice pH = 6.6	200, 250, 300, 350, 400, 450, 500, 550, 600 MPa 100 MPa min^{-1} 0–60 min 5–45 °C	First-order	Van Opstal et al. (2005)

(continued)

Table 3.4 (continued)

Microorganisms	Environment	Processing conditions	Kinetic model	References
Listeria monocytogenes	Fresh, whole, raw milk pH = 6.6	300, 400, 600 MPa 100–200 MPa s^{-1} 0–105 min 25 °C	First-order	Dogan and Erkmen (2004)
	Fresh, filtered orange juice pH = 6.64			
	Fresh, filtered peach juice pH = 3.35			
Native microflora	Unpasteurized Hamlin variety orange juice	350, 400, 450, 500 MPa 1–300 s 25 ± 5 °C	First-order	Parish (1998)
Saccharomyces cerevisae ascospores *Saccharomyces cerevisae* vegetative cells	Commercial pasteurized orange juice			
Vibrio cholerae *Vibrio parahaemolyticus* *Vibrio vulnificus*	Phosphate-buffered saline	200–250 MPa 55–80 s 0–240 s <2 s 8–10 °C (initial)	First-order	Cook (2003)
Bacteriophage P008	Milk	0–800 MPa 10–70 °C 0–60 min	nth order n = 1.25	Müller-Merbach and Hinrichs (2006)

Enzymes	Environment	Processing conditions ranges	Kinetic model	References
a-Amylase (Barley malt (*Hordeum vulgare*))	0.1 M ACES buffer pH 5.6	0–800 MPa 30–90 °C	nth order n = 1.75	Buckow et al. (2007a)
	0.1 M ACES buffer + 3.8 M Ca2+ pH 5.6	0–1000 MPa 30–90 °C	nth order n = 2.1	
Alkaline phosphatase	Raw bovine milk	0–800 MPa 20–100 °C	First order	Ludikhuyze et al. (2000)
β-Amylase (Barley malt (*Hordeum vulgare*))	0.1 M ACES buffer pH 5.6	0–800 MPa 20–80 °C	nth order n = 1.4	Heinz et al. (2005)
β-Glucanase (*Bacillus subtilis*)	0.1 M ACES buffer, pH 5.6	0–1000 MPa 20–80 °C	nth order n = 1.8	Buckow et al. (2007b)
Lipoxigenase (Green pea)	Green peas	0–650 MPa −20–115 °C	First order	Indrawati et al. (2001)
	Supernatant of squeezed green peas			

(continued)

Table 3.4 (continued)

Enzymes	Environment	Processing conditions ranges	Kinetic model	References
Lipoxigenase (Tomato (*Lycopersicom esculentum, cv Malpica*))	Tomato puree	0–750 MPa 5–75 °C	Fractional conversion	Rodrigo et al. (2006)
X-prolyl dipeptidyl aminopeptidase (PepX)	Sodium phosphate buffer solution (pH 7.0)	100–450 MPa 20–40 °C	First order	Giannoglou et al. (2018)
Actinidin (Kiwi fruit)	Solution of phosphate buffer, L-cystein, EDTA and deionized water	0.1, 600, 750, 900 MPa 50–70 °C	First order	Alexandrakis et al. (2017)
Actinidin (Kiwi fruit)	Kiwi fruit juice	200–800 MPa 25–50 °C	First order	Katsaros et al. (2009b)
Ficin (EC 3.4.22.3)	Phosphate buffer 50 mM pH 7.0	500–900 MPa 50–80 °C	First order	Katsaros et al. (2009c)
Papain (EC 3.4.22.2)				
Pectinmethylesterase (Persimmon (*Hachiya cv.*))	Pulp pH 5.5	500–800 MPa 40–70 °C	First order	Katsaros et al. (2006)
Pectinmethylesterase (Sea buckthorn (*Golden sea berry cv.*))	Juice pH 2.8	200–600 MPa 25–35 °C	Fractional conversion	Alexandrakis et al. (2014a)
Pectinmethylesterase (Orange (*Navel cv.*))	Juice pH 3.4	100–800 MPa 30–60 °C	Fractional conversion	Polydera et al. (2004)
Pectinmethylesterase (Orange (*Valencia cv.*))	Juice pH 3.8	100–500 MPa 20–40 °C	Fractional conversion	Katsaros et al. (2010)
Pectinmethylesterase (Orange (*Valencia cv.*)) (Orange (*Navel cv.*))	Tris buffer pH 7.5	200–700 MPa 40–55 °C	First order	Alexandrakis et al. (2014b)
Pectinmethylesterase (Peach (*Everts cv.*))	Phosphate buffer pH 7.0	100–800 MPa 30–70 °C	First order	Boulekou et al. (2010)
Pectinmethylesterase (Carrot (*Daucus carota L. cv.*))	Tris buffer pH 7.0	100–825 MPa 10–65 °C	Fractional conversion	Ly-Nguyen et al. (2003a)
Pectinmethylesterase (Banana (*Cavendish cv.*))	Tris buffer pH 7.0	100–900 MPa 30–76 °C	Fractional conversion	Ly-Nguyen et al. (2003b)
Pectinmethylesterase (Carrot (*D. carota L. cv.*))	Citrate buffer pH 6.0	650–800 MPa 10–25 °C	First order	Balogh et al. (2004)
	Juice pH 6.0	700–800 MPa 10 °C		
	Pieces pH 6.0	700–800 MPa 40 °C		

(continued)

Table 3.4 (continued)

Enzymes	Environment	Processing conditions ranges	Kinetic model	References
Polyphenoloxidase (Pineapple (*Ananas comosus* L.))	Puree pH 3.48	0.1–600 MPa, 30–70 °C 0–20 min	nth order n = 0.991	Chakraborty et al. (2015)
Peroxidase (Pineapple (*Ananas comosus* L.))			nth order n = 0.995	

Food constituents	Environment	Processing conditions ranges	Kinetic model	References
Ascorbic acid	Fresh pineapple juice	0.1–600 MPa 30–95 °C	First order fractional conversion	Dhakal et al. (2018)
Chlorophyll (Broccoli (*Brassica oleracea L. italica*))	Broccoli juice	0–800 MPa 50–105 °C	First order	Van Loey et al. (1998)
Folate (5-methyl-tetrahydropholic acid, 5-CH3-H4-folate)	0.1 M phosphate buffer pH 7.0	0–700 MPa 20–90 °C	First order	Indrawati et al. (2005)
Starch (Normal maize)	5% w/w deionised water	0–700 MPa 20–75 °C	nth order n = 1.65	Buckow et al. (2007c)
Anthocyanins	Raspberry paste	200–700 MPa 90–115 °C	First order	Verbeyst et al. (2011)

Table 3.5 The most common kinetic models used for secondary mathematical modeling for high pressure processing as cited in the literature

Bigelow model	Observations
$Z_p = -P - P_{ref}/\log D_p - \log D_{Pref}$	**Zp or Z_T**: the inverse negative slope of $\log D_P$ or $\log D_T$ versus pressure or temperature level and determines the pressure or temperature increase required to achieve a tenfold increase in the inactivation rate
Model proposed by Santillana Farakos and Zwietering (2011) (based on Bigelow Model)	
$\log D = 1/z_P(P_{ref} - P) + 1/z_T(T_{ref} - T) + 1/z_{PT}[(T_{ref}P_{ref}) - (T_P)] + \log DP_{ref}T_{ref}$	**Z_{PT}** the inverse negative slope of log D_{PT} versus pressure•temperature level and represents the amount that the linear term P·T needs to increase for a tenfold decrease in D
Eyring-Arrhenius Model	
$k(P) = k_{refP}\cdot\exp[-\Delta V^{\neq}(T)/R\cdot(P - P_{ref})T]$ $\Delta V^{\neq}(T) = a\cdot(T - T_{ref}) + \Delta V_T^{\neq}$ $k(T) = k_{refT}\cdot\exp[-Ea(P)/R\cdot(1/T - 1/T_{ref})]$ $Ea(P) = Ea_P\cdot\exp[-g\cdot(P - P_{ref})]$ $k = k_{refP,T}\cdot\exp\{-E_{aP}/R\cdot\exp[-g\cdot(P - P_{ref})]\cdot(1/T - 1/T_{ref}) - a\cdot(T - T_{ref}) + \Delta V_T^{\neq}/R\cdot P - P_{ref}/T\}$	**E_a**: the activation energy **ΔV^***: the activation volume

(continued)

Table 3.5 (continued)

Bigelow model	Observations
Model proposed by Weemaes et al. (1998) (based on Eyring-Arrhenius Model)	
$\ln k_{ref}(P) = c_1 + c_2 \cdot P + c_3 \cdot P^2 + c_4 \cdot P^3$ Weemaes et al. (1998) $E_a(P) = E_{aP} \cdot [\exp(-c_5 \cdot P)]$ $k = \exp\{c_1 + c_2 \cdot P + c_3 \cdot P^2 + c_4 \cdot P^3 + [-E_{aP} \cdot [\exp(-c_5 \cdot P)]R(1/T - 1/T_{ref})]\}$ van den Broeck et al. (2000) $E_a(P) = c_5 - c_6 \cdot P$ $k = \exp\{c_1 + c_2 \cdot P + c_3 \cdot P^2 + c_4 \cdot P^3 + [-c_5 - c_6 \cdot PR(1/T - 1/T_{ref})]\}$	$\mathbf{c_1 - c_4}$: Empirical parameters describe the effect of pressure on k_{ref} Antagonistic pressure effects on k
Model proposed by Ludikhuyze et al. (1998) (based on Eyring-Arrhenius Model)	
$\ln kref(T) = c_1 + c_2 \cdot T + c_3 \cdot T^2$ $\Delta V \neq (T) = c_4 \cdot T \cdot [\exp(-c_5 \cdot T)]$ $\ln k = c_1 + c_2 \cdot T + c^2{}_3 \cdot T - \{c_4 \cdot T \cdot [\exp(-c_5 \cdot T)]/R \cdot T \cdot (P - P_{ref})\}$	Antagonistic effects for combined pressure–temperature treatments for the low-temperature (T < 40 °C) and high-pressure (P > 475 MPa) region
Model proposed by Katsaros et al. (2010) (based on Eyring-Arrhenius Model)	
$k/k_{Tref} = D_{Tref}D_T \cdot 10(T_{ref} - Tz_T)$ $kk_{Pref} = D_{Pref}DP \cdot 10(P_{ref} - Pz_P)$ $D = D_{PrefTref} \cdot \exp\{(P - P_{ref}) \cdot [\Delta V^{\neq}(T)/R \cdot T + 2.303/z_P] + 2.303(T - T_{ref})/z_T + E_a(P)/RT \cdot (1/T - 1/T_{ref})\}$	Proposed for microbial inactivation
Log-logistic model for Weibull distribution	
$\log_{10}(N/N_0) = -b' t^n$ $b'(T) = \ln\{1 + \exp[w_T(T - T_c)]\}^m$ $b'(P) = \ln\{1 + \exp[w_P(P - P_c)]\}^m$ $Pc(T) = P_{c0} \cdot \exp(-w_1 T)$ $Tc(P) = T_{c0} \cdot \exp(-w_2 P)$ $n(P) = d_0 \cdot \exp(-d_1 P)$	T_c: the temperature at which b′ (T) increases linearly for m = 1. If $T > T_c$, the parameter b′ (T) increases to the power $w_T \cdot (T - T_c)$ w_T determines the rate at which b′ (T) increases with temperature. If $T < T_c$, the exponential term tends to zero and b′ (T) is approximately ln (1) = 0

achieve a tenfold increase in the inactivation rate, while the z_T determines the temperature increase required to achieve the tenfold increase in the inactivation rate constant.

The Eyring equation was also developed to mathematically describe the effect of pressure (P) on the inactivation rate constant (k). This effect was correlated to the Activation Volume value (ΔV). Similarly to the Arrhenius equation that is widely used for the mathematical description of temperature on the inactivation rate constant of a quality index. In this case, the Activation Energy (E_a) is estimated and is correlated to the effect of temperature on the inactivation rate constant. In High pressure treatments that pressure and temperature are the main process parameters apart from treatment time, the combined effect of Eyring and Arrhenius equations may be used. Thus, the effects of pressure and temperature may be expressed through the Activation volume and Activation energy, respectively. For more than one different treatment temperatures, the Activation volume value is estimated for each temperature and the effect of temperature on the ΔV values may be estimated

(by plotting ΔV values vs treatment temperatures). The same approach may be followed for the Activation energy as well, that expresses the effect of temperature on the inactivation rate constant of an index. For more than one pressures studied, the E_a value is determined for each pressure and then the effect of pressure on the E_a value can also be determined by plotting the E_a values vs treatment pressures.

Secondary models for the Weibull parameters include a logistic-exponential expression for parameter b', indicating that the inactivation rate constant will be close to zero until a critical pressure level (Pc) is reached. If the pressure level is increased beyond Pc, b′ will increase at a rate w_P. An exponential decay model has been used to predict pressure effects on the Weibull parameter "n", where the dimensionless parameter d_0 is the value of n at pressures P approaching 0, and d_1 is the rate at which n exponentially decays (Doona and Feeherry 2007; Peleg 2006; Doona et al. 2007).

3 Pulsed Electric Field Processing

For PEF treatment, the most critical processing factors are electric field strength, treatment time, shape and width of the pulse, frequency, specific energy, and preheating temperature (Barbosa-Canovas et al. 1999; Wouters et al. 2001). Depending on the conditions intensity, the treatment efficacy is affected leading to microbial population or enzyme activity decrease, causing cell disintegration. The development of mathematical models that can predict the death of microorganisms and inactivation levels of quality-related enzymes by PEF is a very useful tool to design safe and effective PEF processes.

3.1 Primary Mathematical Modeling

Many researchers have focused on developing mathematical models to understand the physiological mechanism of each quality or safety index alteration and how the treatment conditions affected microorganisms, enzymes, quality indices, retention of bioactive compounds and extraction of intracellular compounds from plant tissues. Kinetic models for studying the effects of PEF treatment on the activity of microorganisms or enzymes, have been extensively used in different process conditions and are presented in Table 3.6.

First-order kinetic model as a function of treatment time or electric field strength is the most widely mathematical equation used to describe successfully the effect of PEF treatment on inactivation rate of microorganism, enzymes or retention of health-related compounds in the foods. This model describes the dependency of residual activity of microorganisms or enzymes as a function of the PEF conditions intensity (Bendicho et al. 2002; Giner et al. 2001, 2002, 2003). In literature, the experimental data clearly show an exponentially decrease in residual activity as the

Table 3.6 Mathematical equations cited in the literature and used for the description of the effect of PEF treatment on the value of microbial, enzymatic or chemical reactions

Model	Mathematical equation	Where	References
Kinetic models for the inactivation of microorganisms and enzymes by PEF			
First order kinetic	$RA = e^{-k_P \cdot P}$	RA is the residual activity, P is the studied parameter (PEF treatment time (t, s), electric field strength (E, kV/cm), pulse frequency (f, Hz), the pulse width (τ, s), or the PEF energy input (Q, J/kg)), kP is the inactivation constant rate for the respective studied parameter	Giner et al. (2000, 2001, 2002, 2003)
Empirical Hulsheger's model	$RA = \left(\frac{t}{t_c}\right)^{-\frac{(E-E_c)}{k_c}}$	RA is the residual activity, t is PEF treatment time, E is the electric field strength, E_c, t_c, and k_c are proposed to be independently determined by the target microorganism or enzyme	Hülsheger et al. (1981)
Empirical Fermi model	$RA = \frac{1}{1+e^{\frac{(E-E_c(t))}{a_c(t)}}}$	RA is the residual activity, E is the electric field strength (kV/cm), $E_c(t)$ is the electric field strength (kV/cm) for RA equal to 50% and $a_c(t)$ is the parameter indicating the slope of the curve around E_c. E_c and k_c, are exponentially related to the PEF treatment time t.	Peleg (1995)
Weibull distribution model	$RA = e^{-\left(\frac{t}{a}\right)^{\gamma}}$	RA is the residual activity, P is the studied PEF parameter (treatment time (t, s) or PEF energy input (Q, J/kg)), a and γ are the scale and shape parameters, respectively. Apart from rare exceptions, an exponential relationship exists between the values "a" and electric field strength E	Weibull (1951)
Kinetic models for the extraction of intracellular compounds by PEF			
Empirical Peleg model	$C_t = \frac{t}{k_1 + k_2 \cdot t}$	C_t is the concentration of extracted compound (mg g^{-1}) at time t (s), k_1 is Peleg's rate constant (min g mg^{-1}) and k_2 is Peleg's capacity constant (g mg^{-1})	Peleg (1988)
First-order fractional model	$\frac{C_t - C_\infty}{C_0 - C_\infty} = -k \cdot t$	C_t is the concentration of extracted compound (mg g^{-1}) at time t (s), C_0 is the concentration of extracted compound (mg g^{-1}) at time t = 0, C_∞ is the concentration of extracted compound (mg g^{-1}) at time ∞ time, k is the constant rate of the concentration increase of extracted compound	Levenspiel (1972)

intensity of PEF conditions (electric field strength or treatment time) is increased (Bendicho et al. 2002; Giner et al. 2002). Moreover, the effect of PEF on microbial or enzyme inactivation could also be explained by empirical models such as those of Hülsheger, Fermi's and Weibull distribution model (Table 3.6). These models were first proposed for predicting microbial inactivation, and later to describe the

destruction of enzymes by PEF (Giner et al. 2000; Min et al. 2003). Hülsheger's and Fermi's models describe the decrease of microbial or enzyme activity (RA) as a function of both electric field strength and treatment time.

PEF efficacy is crucial as a knowledge for accepting this technology as a pasteurization process equivalent of thermal treatment. Critical factors affecting microbial inactivation, enzymes inactivation as well as effect on other quality indices is necessary to be studied. The data received from these studies will establish optimized processes that are applicable under a wide range of conditions. Mathematical models applied target to fit microorganism and enzyme responses to processing factors and environmental variables. The fitting accuracy of the traditional first-order kinetics, Hulsheger's, Fermi's, and Weibull distribution models for microbial inactivation by PEF treatments has been reported in several studies (Table 3.7). Similarly to microbial inactivation, effort has been done on the mathematical description of PEF effect on enzymes inactivation. Indicative studies are presented, reporting the mathematical model they applied to describe their results in Table 3.8.

Numerous papers report studies of quality parameters of foods and how are they affected by PEF treatment (Table 3.9). The results obtained are promising, since the health-related compounds and quality indices are retained better when compared to conventional thermal treatment (Min et al. 2003; Odriozola-Serrano et al. 2008a, b).

PEF technology led to retention or enhancement (due to increased extractability offered by PEF technology) of health-related compounds in juices, such as lycopene, vitamin C and polyphenols. Generally, more intense process conditions (higher electric field strength and treatment time), resulted in lower vitamin C (in strawberry as reported by Odriozola-Serrano et al. 2008c, 2009b in tomato reported by Odriozola-Serrano et al. 2007, 2008b, d, 2009a and in watermelon juice cited by Oms-Oliu et al. 2009) and in higher lycopene contents (Odriozola-Serrano et al. 2007) up to 146.2% for tomato juices.

Mathematical description of data obtained by PEF treatment of foods may improve the prediction of the variation of the health-related compounds and antioxidants as affected by key parameters involved in PEF treatments.

PEF was also used to assist and accelerate extraction of high added value compounds from by products, such as tomato peels (Andreou et al. 2020a; Luengo et al. 2014; Pataro et al. 2020), olive pomace (Andreou et al. 2020b), potato peels (Frontuto et al. 2019), grapes by-products (Corrales et al. 2008), orange peels (Luengo et al. 2013), and sesame cake (Sarkis et al. 2015). PEF-assisted extraction could lead to cell alterations or disruption of cell membranes resulting in higher recovery yields of valuable compounds while decreasing the extraction time or solvent volume.

There is limited data in literature about the modeling description of the effect of PEF treatment on the enhancement of mass transfer phenomena. Several researchers have used PEF as pretreatment to conventional extraction procedure and several mathematical models have been used to optimize the PEF conditions' selection.

For instance, Andreou et al. (2020b) used a fractional fist order equation to describe the polyphenol and protein extraction assisted by PEF from olive pomace, and the extracted concentration of each compound was correlated with PEF energy

Table 3.7 Effect of PEF processing conditions range on the inactivation of indicative microorganisms from various food products as cited in the literature

Microorganism	Medium	Process conditions	Maximum reduction (logCFU/g)	Mathematical models	References
E. coli	Orange juice	15–40 kV/cm, pulse width 2.5 μs, treatment time 700 μs, flow rate 60 mL/min, <55 °C	3.83	First order kinetic model Hulsheger's model Weibull distribution model	Rivas et al. (2006)
E. coli O157:H7 Salmonella *Enteriditis*	Liquid egg yolk	30 kV/cm, pulse width 2 μs, treatment time 210 μs, flow rate 12 mL/min, 40 °C	4.9 4.8	First order kinetic model	Amiali et al. (2006)
E. coli CGMCC 1.90	Carrot juice	5–25 kV/cm, pulse width 1.5 μs, treatment time 207–1449 μs, coaxial treatment chamber, flow rate 52.5 mL/min, <40 °C	3.6	Hulsheger's model Fermi's model	Zhong et al. (2005)
Salmonella Dublin (ATCC 15480)	Skim milk	15–40 kV/cm, treatment time 12–127 μs, 10–50 °C	4	Hulsheger's model Fermi's model	Sensoy et al. (1997)
E. sakazakii CECT 858	Buffered peptone water Rehydrated infant formula milk	10–40 kV/cm, pulse width 2.5 μs, treatment time 360 μs, flow rate 1.8 L/h, 25 °C	2.7 1.7	First order kinetic model Weibull distribution model	Pérez et al. (2007)
Salmonella Senftenberg 775 W	Liquid whole egg	20–45 kV/cm, square pulse width 3 μs, treatment time 0–150 μs, 55 °C	3.3	Weibull distribution model	Monfort et al. (2010)
E. coli *L. monocytogenes*	Melon & watermelon juice	35 kV/cm, pulse width 4 μs, pulse frequency 217 Hz, treatment time 1440 μs, 40 °C	3.7 3.56 3.6 3.41	Quadratic response model	Mosqueda-Melgar et al. (2007)

(continued)

Table 3.7 (continued)

Microorganism	Medium	Process conditions	Maximum reduction (logCFU/g)	Mathematical models	References
E. coli *O157:H7* *Salmonella* *Enteriditis*	Apple Pear Orange Strawberry juice	35 kV/cm, bipolar pulse width 4 μs, flow rate 80–110 mL/min, <40 °C	4.29 4.34 4.59 4.87 5.16 5.22 5.56 4.43	Quadratic response model	Mosqueda-Melgar et al. (2008)
G. oxydans *K. apiculata* *L. bacteria* *S. cerevisiae*	Grape juice	35 kV/cm, bipolar pulse width 5 μs, pulse frequency 303 Hz, flow rate 3.33 mL/s, inlet temperature 15 °C, maximum temperature <30.4 °C	2.24 3.88 3.54 3.90	Quadratic response model	Marsellés-Fontanet et al. (2009)

Table 3.8 Effect of PEF processing conditions range on the inactivation of indicative enzymes from various food products as cited in the literature

Enzyme	Medium	Process conditions	Residual activity (%)	Mathematical models	References
LOX	Tomato juice	35 kV/cm, pulse width 3 μs, 50 μs treatment time, flow rate 1 mL/s, 30 °C	20	First order kinetic model Hulsheger's model Fermi's model Quadratic response model	Min et al. (2003)
PME	Tomato juice	5–24 kV/cm, 10.9–108.0 MJ/m^3 energy input, pulse width 0.02–0.04 ms, 0–400 pulses	8	First order kinetic model Hulsheger's model Fermi's model	Giner et al. (2000)
LOX	Tomato juice	35 kV/cm, 250 Hz, bipolar pulse width 7 μs, treatment time, 1000 μs	81	Quadratic response model	Aguiló-Aguayo et al. (2009a)
PME PG	Tomato juice	5.5–12.5 kV/cm, 0–12 ms treatment time, pulse width 15 μs, 300 Hz, bipolar pulses	98 45	First order kinetic model	Andreou et al. (2016)

(continued)

Table 3.8 (continued)

Enzyme	Medium	Process conditions	Residual activity (%)	Mathematical models	References
PME PG POD	Tomato juice	35 kV/cm, 250 Hz bipolar pulse width 7 μs, flow rate 60 mL/min	10 45 0	Quadratic response model	Aguiló-Aguayo et al. (2008a, b, 2009a, b)
LOX	Soymilk	20–40 kV/cm, 400 Hz pulse width 2 μs, treatment time 1036 μs, 25 °C	12	First order kinetic model Fermi's model Weibull distribution model	Li et al. (2008)
PME	Orange juice	25 kV/cm, 700 Hz pulse width 2.0 ms, flow rate 0.31 mL/s, 50 °C	10	First order kinetic model	Yeom et al. (2002)
PME	Orange juice	5–35 kV/cm, 200 Hz bipolar and monopolar pulse width 4 μs, treatment time 1500 μs, 60 mL/min, 37.5 °C	20	First order kinetic model Hulsheger's model Fermi's model Weibull distribution model	Elez-Martinez et al. (2007)
PME	Fresh mixed orange and carrot juice	25–40 kV/cm, bipolar pulse length 2.5 μs, treatment time 340 μs, 60 mL/min	18.6	First order kinetic model Hulsheger's model Weibull distribution model	Rodrigo et al. (2003)
PME	Red grape juice	40 kV/cm, 15 Hz pulse width 1 μs, treatment time 100 μs	3.2	First order kinetic model	Riener et al. (2009)
POD, PPO	Grape juice	25–35 kV/cm, 600 Hz bipolar pulse width 4 μs, treatment time 5 ms, flow rate 7.8 mL/s, 40 °C	49.4 0	First order kinetic model	Marsellés-Fontanet and Martin-Belloso (2007)
POD, PPO	Grape juice	25–35 kV/cm, 600 Hz bipolar pulse width 4 μs, treatment time 5 ms, flow rate 7.8 mL/s, 40 °C	49.4 0	Quadratic response model	Marsellés-Fontanet and Martin-Belloso (2007)
POD, PPO	Apple juice	23–50 kV/cm, 15 Hz pulse width 1 μs, treatment time 100 μs, 50 °C	32, 29	First order kinetic model	Riener et al. (2008)

(continued)

Table 3.8 (continued)

Enzyme	Medium	Process conditions	Residual activity (%)	Mathematical models	References
PPO	Apple & pear	22.3–24.6 kV/cm, up to 6 ms treatment time, bipolar mode, exponential decay pulses, 0.02 ms pulse width	96.8 62.0	First order kinetic model	Giner et al. (2001)
PPO	Peach juice	24.3 kV/cm, bipolar pulse width 0.02 ms, 5 ms treatment time	30	First order kinetic model	Giner et al. (2002)
PME, PG	Strawberry juice	35 kV/cm, 100 Hz monopolar pulse width 1 μs, flow rate 60 mL/min	10, 75	Quadratic response model	Aguiló-Aguayo et al. (2009a)
LOX, POD	Watermelon juice	35 kV/cm, 50 Hz monopolar pulse width 1 μs, treatment time 1000 μs	112.25 15.25	Quadratic response model	Aguiló-Aguayo et al. (2010)
PME	Gazpacho	35 kV/cm, 200 Hz monopolar pulse width 4 μs, treatment time 1500 μs, flow rate 60 mL/min, 40 °C	3.8	Giner-Segui's model	Giner-Seguí et al. (2009)

input. Moreover, lycopene extraction kinetic from industrial tomato peels was well fitted by Peleg's model (Pataro et al. 2020), allowing to select the optimal PEF conditions with low energy consumption.

3.2 Secondary Mathematical Modeling

Except on empirical models that are used as a first step to obtain optimum values of each factor with maximal reduction for every microorganism or enzyme, there is no secondary modeling approach proposed in the literature. This is mainly attributed to the numerous process parameters that counteract between them not allowing for development of secondary models.

4 Pulsed Electromagnetic Fields Processing

Pulsed electromagnetic fields (PEMF) technology involves the generation and powerful direction of pulsed electromagnetic waves. The generated waves seem to react with the cells that come in contact changing the state of the electrons spin system

Table 3.9 Effect of PEF processing conditions range on the effect of quality indices of various food products as cited in the literature

Quality and bioactive compounds	Medium	Process conditions	RC	Mathematical models	References
Anthocyanin Vitamin C Antioxidant capacity	Strawberry juice	25–35 kV/cm, 232 Hz bipolar pulse width 1 μs, 100 μs treatment time, flow rate 60 mL/min, 40 °C	100.5 93 0	First order kinetic model Weibull distribution model	Odriozola-Serrano et al. (2008c)
Antioxidant capacity Vitamin C	Tomato juice	35 kV/cm, 100 Hz bipolar pulse width 4 μs, 1500 μs treatment time, flow rate 60 mL/min, 40 °C	0	First order kinetic model	Odriozola-Serrano et al. (2008b)
Antioxidant capacity Lycopene Vitamin C	Tomato juice	35 kV/cm, 250 Hz bipolar pulse width 1 μs, 500 μs treatment time, flow rate 60 mL/min, 40 °C	137.7 100 97	Weibull distribution model Fermi's model First order kinetic model	Odriozola-Serrano et al. (2008d)
Ascorbic acid	Milk	A static parallel plate treatment chamber, 27.1 kV/cm, 20–25 °C	93.4	First order kinetic model	Bendicho et al. (2002)
Anthocyanin Vitamin C	Strawberry juice	35 kV/cm 250 Hz, bipolar pulse width 1 μs, treatment time 1000 μs	101.9 100.3	Quadratic response model	Odriozola-Serrano et al. (2009b)
Antioxidant capacity Lycopene Vitamin C	Tomato juice	35 kV/cm, 150 Hz bipolar pulse width 4 μs, 1000 μs treatment time, flow rate 60 mL/min, 40 °C	92.3 146.2 99	Quadratic response model	Odriozola-Serrano et al. (2007)
Antioxidant capacity Lycopene Vitamin C	Watermelon juice	35 kV/cm 200 Hz, bipolar pulse width 7 μs, treatment time 50 μs	100 72 113	Quadratic response model	Oms-Oliu et al. (2009)

(Pawluk 2015). PEMF is mainly studied for its use for human therapeutic purposes, indicating significant effects on cells, tissues and biological processes such as embryogenesis, regeneration, wound healing (Hammerick et al. 2010), as well as in cell migration, DNA synthesis and gene expression (Tsai et al. 2009; Luo et al. 2012; Kang et al. 2013). PEMF technology has hardly been studied for its effect on food products, however it is considered to be a promising technology for microbial inactivation (Tadevosian et al. 2006; Torgomyan et al. 2011; Giannoglou et al. 2020a, 2021). Extensive work on the effect of PEMF on a food system (whole fresh strawberries) has been performed by Giannoglou et al. (2021). PEMF processing did not appear to have a significant impact on the weight loss, the color, the total anthocyanin content and on the pH-value of the strawberries, after processing and

during storage. PEMF processing led to a 16% decrease in the firmness of the strawberries immediately after processing compared to Control samples, which was also maintained during storage. A significant increase in the total phenolic content and in the free radical scavenging activity was observed for PEMF processed fruits immediately after processing. PEMF processed strawberries also presented higher peak values in the total phenolic content during storage compared to the untreated ones. The PEMF strawberries presented the highest values in ascorbic acid content after processing and also during storage, compared to Control. PEMF technology could be used for enhancement of nutritional value of fruits in addition to the quality retention related with safety and consumer perceived traits. Nevertheless, there has not yet been described the effect of PEMF on any quality index by mathematical equations. There is a lot of space for work towards this direction, since the equations applied for PEF treatments could be modified and applied also for PEMF treated food products.

5 Cold Atmospheric Plasma Processing

Cold atmospheric plasma (CAP) is an emerging non-thermal processing method that attracts an ever increasing interest for future application in food industry (Schlüter et al. 2013; Niemira 2012; Giannoglou et al. 2020a, b). Plasma is a partially ionized gas consisting of a reactive mixture of charged particles, free radicals, excited species, and UV photons. Novel plasma reactor designs and electrical power supplies have enabled the generation of non-thermal, far from thermodynamic equilibrium, plasmas in atmospheric pressure (Pappas 2011; Brandenburg 2018). The high reactivity combined with the low temperature operation render plasma suitable for treatment of heat-sensitive food products, due to their ability to deactivate microorganisms (Kelly-Wintenberg et al. 1999; Moisan et al. 2002; Laroussi 2005; Puač et al. 2017; Dimitrakellis et al. 2021). In the field of fruits, the investigation mainly concerns the CAP effect on the microorganisms/enzymes and quality characteristics of fruit products such as orange juice (Xu et al. 2017), white grape juice (Pankaj et al. 2017), siriguela juice (Paixão et al. 2019), fresh-cut apples (Ramazzina et al. 2016; Tappi et al. 2014), fresh-cut melon (Tappi et al. 2016). A more limited number of studies concern the effect of this technology on whole fruit i.e. blueberries (Sarangapani et al. 2017) and cherry tomatoes (Misra et al. 2014). Studies on the effect of CAP processing on quality parameters of whole fruits during storage are limited to strawberries (Rana et al. 2020; Giannoglou et al. 2021) and mandarins (Won et al. 2017). Based on the reported results, CAP processing induced the inactivation of microorganisms mostly due to the interaction with reactive oxygen and nitrogen species (RONS) generated in the gas phase during processing. The effect of plasma treatment on the quality characteristics varied from significant to insignificant, depending on the investigated parameters, the product characteristics, as well as the intensity of the processing and the plasma source design. Indirect plasma treatment of strawberries through immersion in plasma activated water has also

Table 3.10 Indicative mathematical equations cited in the literature and used for the description of the effect of CAP treatment on the value of microbial and enzymatic reactions

Model	Mathematical equation	Where	References
First-order model	$\ln A/A_0 = -k \cdot \Delta t$	Where A_0 is the initial activity of PPO, A represents the PPO activity at time t, k is the first-order kinetic constant (min^{-1}), and t is the treatment time (min).	Dong et al. (2021); Liang et al. (2012)
Weibull model	$\ln A/A_0 = -(t/a)^{\beta}$	Where A and A_0 have the same meaning as in Eq. (2), t is the DBD plasma exposure time (min), α is the scale parameter (characteristic time, min), and β is the shape parameter. The β value denotes an idea of the form of the inactivation curve: upward concavity ($\beta < 1$), straight line ($\beta = 1$), or downward concavity ($\beta > 1$).	Dong et al. (2021); Liang et al. (2012)
Logistic model	$A = [(100 - A_{min})]/[1 + (t/t_{50})^p] + A_{min}$	Where A_{min} (≥ 0) is the minimum value attained by the logistic function, t_{50} is the time of half-maximal activity (min), and p is the power term.	Pankaj et al. (2013); Dong et al. (2021)

been proposed in the literature for efficient disinfection based on secondary RONS formed in liquid phase upon interaction with gas discharges (Ma et al. 2015).

In general, CAP can be used either as direct (direct processing of a food product by the ionized gas), semi-direct (surface dielectric barrier discharge used for the treatment of whole food products) or even indirect (production of "plasma activated water" and immersion of food products within this water rich in Reactive Oxygen Nitrogen Species with the antimicrobial effect) applications. In all cases, there is limited work done on the mathematical description of the data obtained. This is mainly attributed to the numerous process parameters for CAP treatment making it harder for the researchers to apply or develop appropriate mathematical equations. Nevertheless, the models applied in the limited works cited in the literature are depicted in Table 3.10. No secondary models have been applied or developed for the description of the effect of process parameters on the inactivation rate constants for microbial, enzymatic and chemical indices.

The works having included the kinetic approach in data obtained by applying the Cold Atmospheric Plasma technology on microbial, enzyme and chemical indices are very limited and some of them are depicted in Table 3.11. The Weibull model is mainly used by the researchers both for microbial and enzymatic inactivation.

6 Osmotic Dehydration

Osmotic dehydration (OD) has received greater attention in recent years as an important complementary treatment and food preservation technique in the processing of dehydrated foods. OD is a water removal process which is based on the implementation of foods, mainly fruits and vegetables, in a hypertonic solution,

Table 3.11 Effect of CAP processing conditions range on the effect of indicative microorganisms, enzymes and quality indices of various food products as cited in the literature

Model	Process conditions	Medium	Reference
Weibull model	Dielectric barrier discharge-atmospheric cold plasma treatment at high voltages (40, 50 and 60 kV) for durations ranging between 15 s and 5 min	Alkaline phosphatase enzyme	Segat et al. (2016)
Weibull model	Fixed distance of 35 mm, input power of 200 W for 30, 60, 120, 180, and 240 s	Salmonella and Escherichia coli in apples	Kilonzo-Nthenge et al. (2018)
Weibull model	Plasma exposure time varied between 0 and 480 s. The gas flow rate was 5 slm (standard litre per minute), and the power supply was operated at a voltage of 65 V and a resonance balancing of 0.05 A. The distance between nozzle outlet and sample was set to 10 mm.	*Citrobacter freundii* in apple juice	Surowsky et al. (2014)
Weibull model and a three-parameter logistic model	Different voltages (30, 40 and 50 kV) for different time intervals (15 s–5 min)	Tomato POD inactivation	Pankaj et al. (2013)
Weibull and logistic model	Different voltages (18, 23 and 28 kV) for different time intervals (15 s–5 min)	Peroxidase and polyphenol oxidase in tender coconut water	Chutia et al. (2019)
Weibull and logistic model	19.4, 26.4, and 32.6 W, for 3 min	PPO isolated from *Agaricus bisporus*	Dong et al. (2021)
Weibull model	50 kV (65–75 W @ 0.5–0.8 mA) with an electrode gap or depth of 2.5 cm. Samples exposures time to the cold plasma discharge were 0, 15, 30, 60, and 120 s.	B. subtilis spores	Mendes-Oliveira et al. (2019)

reducing its water content while increasing the soluble solid content. The raw material is placed in concentrated solutions of soluble solids with higher osmotic pressure and lower water activity. Diffusion phenomenon takes place with two countercurrent flows: a water flow from the food to the outer solution and a simultaneous flow of solute from the solution to the food (de Mello Jr et al. 2019), enriching its composition by enhancing its nutritional value. These mechanisms lead to water loss and solid gain in the food. OD process occurs at mild temperatures (<50 °C), thus low energy consumption and processing costs are required (Torreggiani 1993). Although OD process will not give a product of sufficiently low moisture content to be considered a shelf stable product and therefore, OD should be combined with other preservation techniques.

The kinetics of mass transfer is described using terms such as water loss (WL), solids or solutes gain (SG) and water activity (a_w) reduction (Pękosławska and Lenart 2009). The most important variable markedly affecting the kinetics of mass

transfer during OD is temperature (Mokhtarian et al. 2014). This enhances the removal of water and uptake of solids.

The most widely used model for OD processes at atmospheric pressure is the Crank's model, which consists of a solution of non-steady Fick's law and represents the diffusional mechanism. Crank's model (Crank and Gupta 1975) consists of a group of analytical solutions of Fick's diffusion law that were obtained by Crank for various geometries and several initial and boundary conditions. Other models can also be found in the literature trying to describe the effect of process parameters on the mass transfer phenomena and are presented in Table 3.12.

Many researchers used the Crank's model in order to describe the mass transfer phenomena during OD treatment of various tissues such as apple (Sereno et al. 2001), strawberry (Dermesonlouoglou et al. 2017a), goji berry (Dermesonlouoglou et al. 2018), tomato (Dermesonlouoglou et al. 2017b), cucumber (Dermesonlouoglou et al. 2008), kiwi (Dermesonlouoglou et al. 2016), pumpkin (Dermesonlouoglou et al. 2020), apricot (Dermesonlouoglou et al. 2019a; Dermesonlouoglou and Giannakourou 2018), bananas (Mercali et al. 2010), etc. The effective diffusivities of water and solids were found to be in the range of $2.0 \pm 1.0 \times 10^{-7}$ to $0.7 \pm 0.2 \times 10^{-11}$ m^2/s, depending on the food tissue and the OD treatment conditions applied.

OD is the process that can be used as pre-treatment for conventional drying procedures, such as air-drying, microwave-drying and freeze drying. High temperature and long drying time in conventional drying may change flavor, color and rehydration capacity of dried products (Garcia et al. 2007). In all cases the drying efficiency and energy demand is associated with drying time, which is highly related with volume of moisture in a material to be removed or the rate at which drying can be accomplished. As a pretreatment it is necessary for the food engineer to effectively predict the effect of OD on quality indices, so as not to over process the food product. Thus, kinetic modeling is essential and can provide useful information on the necessary treatment conditions, depending on the tissue to be treated. Several researchers have studied and mathematically modeled the use of OD as a pretreatment to air-drying for fruits and vegetables such as tomato and cucumber (Dermesonlouoglou et al. 2019b), goji berry (Dermesonlouoglou et al. 2018), apple (Mandala et al. 2005), banana (Fernandes et al. 2006), pumpkin (Garcia et al. 2007) and melon (Teles et al. 2006). The beneficial use of OD has also been demonstrated for dairy (Giannoglou et al. 2020c) and meat products (Andreou et al. 2018).

7 Models Application, Process Parameters Estimation and Validation

The development and application of predictive models for the description of the effect of Nonthermal process conditions on safety and quality indices is a very useful tool for the food engineers and food scientists in general. These models already

Table 3.12 Mathematical equations cited in the literature and used for the description of the effect of OD treatment on the value of mass transfer phenomena

Model	Equation	Where
Crank's model: Semi-infinite plane	$M_{OD} = \frac{(m_t - m_\infty)}{(m_0 - m_\infty)} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[-\left(n+\frac{1}{2}\right)^2\pi^2 D_{ew}\frac{t}{l^2}\right]$ $S_{OD} = \frac{(s_t - s_\infty)}{(s_0 - s_\infty)} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[-\left(n+\frac{1}{2}\right)^2\pi^2 D_{es}\frac{t}{l^2}\right]$	M and S are the diffused moisture and solute ratio, respectively, m and s are the moisture and solute content, the subscripts o, t and ∞ represent the relevant values at time 0, t and at equilibrium, D_{ew} and D_{es} (m^2/s) are the effective coefficients of water and solute diffusivity, respectively, l (m) is the half thickness of the slab.
Crank's model: Sphere	$M_{OD} = \frac{(m_t - m_\infty)}{(m_0 - m_\infty)} = \frac{6}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{n^2}\exp\left[n^2\pi^2 D_{ew}\frac{t}{a^2}\right]$ $S_{OD} = \frac{(s_t - s_\infty)}{(s_0 - s_\infty)} = \frac{6}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{n^2}\exp\left[n^2\pi^2 D_{ew}\frac{t}{a^2}\right]$	M and S are the diffused moisture and solute ratio, respectively, m and s are the moisture and solute content, the subscripts o, t and ∞ represent the relevant values at time 0, t and at equilibrium, D_{ew} and D_{es} (m^2/s) are the effective coefficients of water and solute diffusivity, respectively, a (m) is the radius of the sphere.
Crank's model: Rectangular parallelepiped	$M = \frac{m_t - m_\infty}{m_0 - m_\infty} = \sum_{n=1}^{\infty} C_n^3 \exp\left[-D_{ew} q_n^2 t\left[\left(\frac{1}{a^2}\right)+\left(\frac{1}{b^2}\right)+\left(\frac{1}{c^2}\right)\right]\right]$ $S = \frac{S_t - S_\infty}{S - S_\infty} = \sum_{n=1}^{\infty} C_n^3 \exp\left[-D_{es} q_n^2 t\left[\left(\frac{1}{a^2}\right)+\left(\frac{1}{b^2}\right)+\left(\frac{1}{c^2}\right)\right]\right]$	M and S are the diffused moisture and solute ratio, respectively, m and s are the moisture and solute content, the subscripts o, t and ∞ represent the relevant values at time 0, t and at equilibrium, D_{ew} and D_{es} (m^2/s) are the effective coefficients of water and solute diffusivity, and C_n was equal to 2a(1 + a)/(1 + a + a2qn2), where qn's were the positive roots other than zero of equation: tan(qn) = −αqn. α was the ratio of the volume of the osmotic solution to that of piece, a, b, c are the dimensions of parallelepiped.

(continued)

Table 3.12 (continued)

Model	Equation	Where
Crank's model: Cube	$M = \frac{m_t - m_\infty}{m_0 - m_\infty} = \sum_{n=1}^{\infty} \frac{2 \cdot a \cdot (1+a)}{1 + a + a^2 \cdot q_n^2} \exp\left(\frac{D \cdot q_n^2 \cdot t}{l^2}\right)$ $S = \frac{S_t - S_\infty}{S - S_\infty} = \sum_{n=1}^{\infty} \frac{2 \cdot a \cdot (1+a)}{1 + a + a^2 \cdot q_n^2} \exp\left(\frac{D \cdot q_n^2 \cdot t}{l^2}\right)$	M and S are the diffused moisture and solute ratio, respectively, m and s are the moisture and solute content, the subscripts o, t and ∞ represent the relevant values at time 0, t and at equilibrium, D_{ew} and D_{es} (m^2/s) are the effective coefficients of water and solute diffusivity, and C_n was equal to 2a(1 + a)/(1 + a + a2qn2), where qn's were the positive roots other than zero of equation: tan(qn) = −αqn. α was the ratio of the volume of the osmotic solution to that of piece, l is the edge of the cube
Magee's Model	$WL \text{ or } SG = kt^{0.5} + k0$	k and k0 are empirical kinetic parameters. k is associated with the transfer rates of water and solute that occur through the osmotic-diffusional mechanism, and k0 with the gain or loss of mass that occurs after very short processing times due to the action of the hydrodynamic mechanism promoted by imposed or capillary pressures.
Peleg's model	$WL_t = WL_0 + \frac{t}{k_1 + k_2}$ $SG_t = SG_0 + \frac{t}{k_1 + k_2}$	WL and SG are the amount of water loss or solids gain at time t, g; WL_0 and SG_0 are the initial amount of water or solids, g; k_1 and k_2: Peleg's constants; and t is the time, h.
Page's model	$M = \frac{m_t - m_\infty}{m_0 - m_\infty} = \exp\left(-At^B\right)$	m and s are the moisture and solute content, the subscripts o, t and ∞ represent the relevant values at time 0, t and at equilibrium, A and B are the Page's water loss or solid gain parameters
Newton model	$M = \frac{m_t - m_\infty}{m_0 - m_\infty} = \exp\left(-k_1 t\right)$	m and s are the moisture and solute content, the subscripts o, t and ∞ represent the relevant values at time 0, t and at equilibrium, k_1 is the Newton parameter

Model	Equation	Where
Henderson–Pabis	$M = \frac{m_t - m_\infty}{m_0 - m_\infty} = a \cdot \exp(-k_2 t)$	m and s are the moisture and solute content, the subscripts o, t and ∞ represent the relevant values at time 0, t and at equilibrium, k_2 and a are the Henderson–Pabis parameters
Azuara model	$\frac{t}{WL} = \frac{1}{s1(WL_\infty)} + \frac{t}{WL_\infty}$ $\frac{t}{SG} = \frac{1}{s1(SG_\infty)} + \frac{t}{SG_\infty}$	WL or SGt, ∞: Water loss or solid gain fraction at any time, t or at equilibrium s_1 and s_2 are parameters that can be defined as relative rate constants for moisture loss and solid gain, respectively.

developed by food scientists and researchers allow for the scaling up of Nonthermal processes. Industry food engineers can adopt these equations and effectively apply them for predicting the optimal process conditions for the products to be treated. This does not require any special skills from the food engineer, neither a special tool, apart from a common software (Excel, Sigmaplot, SYSTAT, Origin softwares etc.) already installed to most PCs.

The food engineer will have to transfer the equation to one of the softwares and by replacing the model parameters with the ones estimated by scientists after numerous experiments will be able to predict the total effect on microbial, enzymatic or chemical indices (depending on the dominant deterioration factor) allowing him to decide which process conditions are more appropriate and efficient for the production.

Of course, since the models are just equations, there is always an error in the predictions, thus the food engineer has to validate the results obtained in his/her PC by results obtained from the actual production considering the process parameters estimated by the models. The deviation between predicted and observed values (effect on safety and quality indices after the processing) must not be high otherwise the model cannot predict with high accuracy and cannot be used for the scale up of processes.

8 Application of Kinetic Modeling for Process Optimization and Case Studies

Two cases studies on how a food engineer could work and take advantage of the kinetic approach and the predictions by the kinetic models on selecting the optimal process conditions are presented below. Both case studies concern the application of High pressure technology on the cold pasteurization of orange juices of different varieties; the first one is Valencia var., while the second one is Navel var.

The dominant quality indices that were taken into consideration are the dominant microbial flora-Lactic acid bacteria, LAB (*L. plantarum* and *L. brevis*) and the endogenous enzyme pectinmethylesterase that causes cloud loss, thus quality degradation of the juices. For both cases, a wide range of experiments on inactivating these indices by high pressure was conducted. The data received were mathematically described by the combined Eyring-Arrhenius equation, used to predict the inactivation rate constants at any combination of pressure and temperature for both juices. By estimating the inactivation rate constants, the necessary processing time can be determined for achieving a stable final food product. Iso-reduction plots for achieving a seven microbial log reduction and 90% PME inactivation after High processing were developed.

8.1 Case Study 1: Valencia Orange Juice

The Fig. 3.2 depicts the necessary combination of pressure and temperature process conditions for achieving the seven microbial log reduction and 90% PME inactivation, after 2 and 5 min processing time, conducted by Katsaros et al. (2010). By the obtained results, the food engineer may select the necessary process conditions for optimal high pressure processing, avoiding over-processing and products degradation or not sufficient processing for pasteurization thus survival of degradation factors. Process conditions required for the simultaneous targeted inactivation of PME and LAB in 5 min are 325 MPa and 30 °C. More intense process conditions (360 MPa and 35 °C) are required for 2 min processing.

8.2 Case Study 2: Navel Orange Juice

Similarly to the case study 1, the authors of this current chapter have unpublished data showing the iso-reduction plots for achieving a seven microbial log reduction and 90% PME inactivation after processing for 3 and 5 min for another orange juice variety, the Navel cv. one. *Lactobacillus plantarum* appeared to be relatively sensitive to pressures above 300 MPa. Navel orange PME sensitivity is in accordance with the general statement that PMEs are generally more resistant than microorganisms and that treatment for PME inactivation is sufficient for juices pasteurization. For Navel orange juice pasteurization, inactivation of 90% of the pressure/temperature labile PME fraction was considered as process target. For LAB a 7D reduction of the most resistant strain was considered. The required processing times for pasteurization of Navel orange juice PME at different process pressures, at 25 and 30 °C are shown in Fig. 3.3. Processing at 25 and 30 °C requires longer times for the PME inactivation compared to the inactivation of LAB species. The necessary pressure and temperature process conditions for the inactivation of 90% PME and 7D LAB reduction were estimated for 5 min (milder conditions are required) and 3 min (more intense treatment conditions are required) processing time. The microbial and enzymatic iso-reduction contour plots for achieving 90% PME inactivation and seven microbial log reductions after processing for 5 and 3 min are depicted in Fig. 3.4.

According to the above results, the selection of HP processing conditions was based mainly on PME inactivation. A treatment of fresh Greek Navel orange juice at 600 MPa and 40 °C for 3 min can cause inactivation of the labile isoenzyme, leading to a remaining PME activity equal to approximately 10% of the initial activity of untreated juice. These conditions also exceeded process requirements for microbial stability of orange juice.

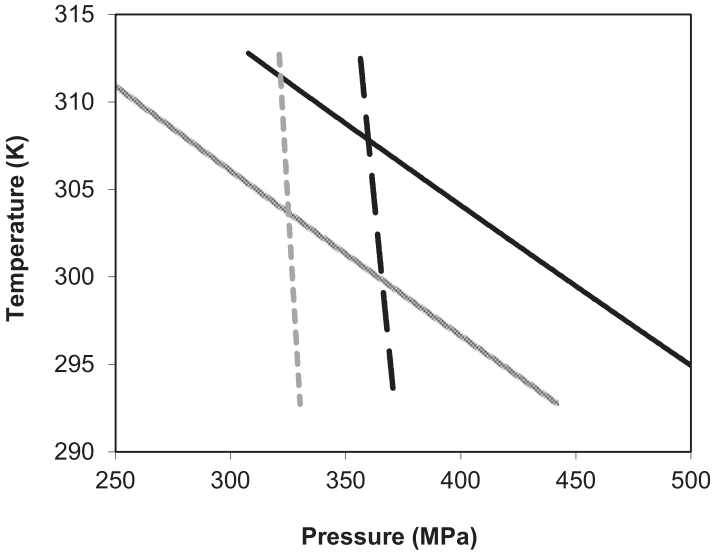

Fig. 3.2 Microbial (LAB) and enzymatic (PME) iso-reduction plots for achieving a seven microbial log reduction and 90% PME inactivation after processing for 2 and 5 min. Dashed lines represent a 7D LAB destruction and solid lines represent 90% PME inactivation. Black lines show processing for 2 min, while grey lines show processing for 5 min (own data, as published to Katsaros et al. 2010)

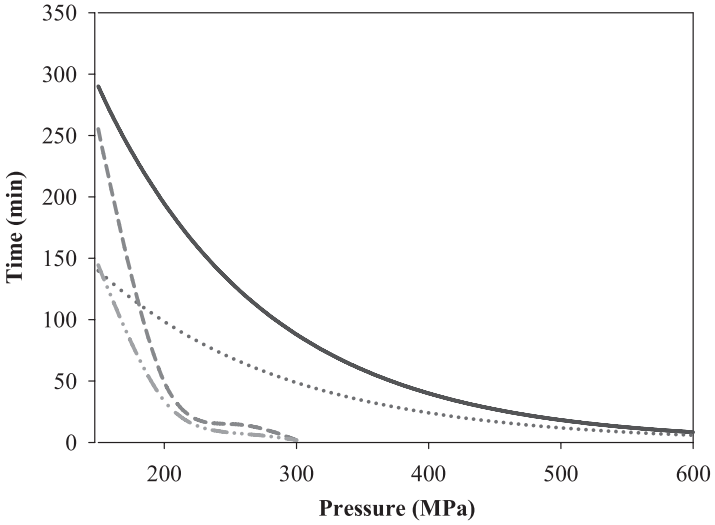

Fig. 3.3 Required processing time for the inactivation of PME and LAB as a function of pressure at 25 and 30 °C. Solid and dotted lines represent 90% PME inactivation at 25 °C and 30 °C, respectively. Dashed and dash-double dotted lines represent 7D LAB reduction at 25 °C and 30 °C, respectively

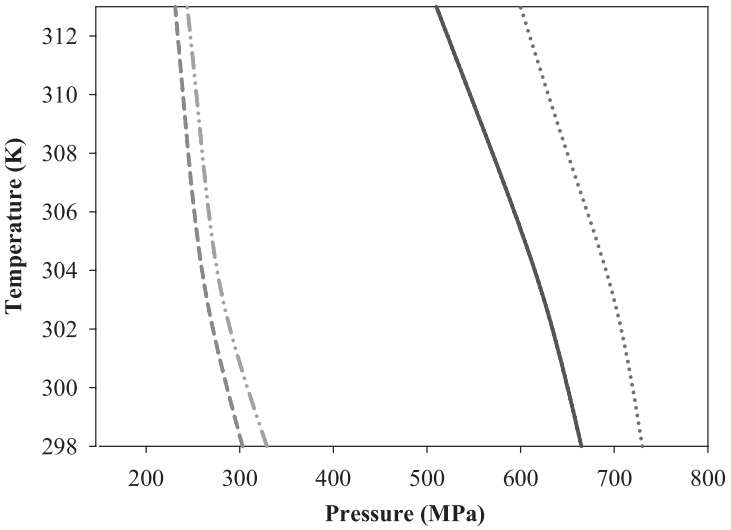

Fig. 3.4 Microbial (LAB) and enzymatic (PME) iso-reduction plots for achieving a seven microbial log reduction and 90% PME inactivation after processing for 3 and 5 min. Solid and dotted lines represent 90% PME inactivation after processing for 3 and 5 min, respectively. Dashed and dash-double dotted lines represent 7D LAB reduction after processing for 3 and 5 min, respectively

9 Conclusions and Future

In general, kinetic modeling is essential in nowadays for achieving an efficient processing in terms of producing food products of increased safety, quality, healthier profile while simultaneously being more cost effective. The scientists have done a lot of work towards producing data necessary for the development of mathematical equations for the description of the effect of process conditions with Nonthermal technologies on quality indices of new or improved food products. Nevertheless, there is space for more work on developing more reliable models with not significant errors, thus of higher accuracy when using them to scale up production from the labs to the industries. New measuring techniques providing more reliable values will boost the applicability and efficiency of kinetic models.

Nonthermal technologies are the future of food processing, but some issues related to products specificity have to be taken into consideration. Food engineers will have in their hands useful tools to predict optimal process conditions, thus evaluate for the process applied, its intensity and efficiency, enabling the use of corrective actions if needed, for production of safe, sustainable and cost-efficient final food products. Training and education has to be improved towards this direction enabling for the food engineers to efficiently take advantage of the tools-kinetic models available in the literature.

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