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Convergence of Bigelow and Arrhenius models over a wide range of heating temperatures

Stéphane André[a,*], Ivan Leguerinel[b], Alfredo Palop[c], Noémie Desriac[b], Stella Planchon[a], Pierre Mafart[b]

[a] Centre Technique pour la Conservation des Produits Agricoles (CTCPA), Unité Expertise dans la Maîtrise du Risque Industriel en Thermorésistants Sporulés (EMaiRITS), 449 avenue Clément-Ader, 84911 Avignon, France
[b] Université de Brest, EA3882, Laboratoire Universitaire de Biodiversité et Ecologie Microbienne, UMT14.01 SporeRisk, 6 rue de l'Université, F-29334 Quimper, France
[c] Departamento Ingenieria de Alimentos y del Equipamiento Agrıcola, Campus de Excelencia Internacional Regional "Campus Mare Nostrum", Universidad Politecnica de Cartagena, Paseo Alfonso XIII, 48, 30203 Cartagena, Spain

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ABSTRACT

The heat resistance of the bacterial spores of *Moorella thermoacetica*, *Clostridium sporogenes*, *Geobacillus stearothermophilus* and *Bacillus coagulans* was determined over a wide range of temperatures using the capillary method and thermoresistometer Mastia. The results showed that the two experimental methods gave similar heat resistance values excepted for *Geobacillus stearothermophilus*.

The effect of temperature on thermal resistance was evaluated using the Arrhenius and Bigelow models. The fit of the heat sensitivity parameters of the Arrhenius and Bigelow models on the heat resistance parameter values obtained over a wide temperature range was equally good. Despite the apparent mathematical incompatibility of the two equations, it is recognized that they yield the same goodness of fit. This paper finds a mathematical reason for this convergence and explains why inside a temperature range of at least 100 °C, no significant difference in the quality of fit between these two models can be found.

1. Introduction

Heating is a conventional method for inactivation of microorganisms. The optimization of pasteurization or sterilization processes uses mathematical models to calculate the heating temperature and time to reduce microbial populations or completely inactivate highly heat resistant microorganisms such as bacterial spores responsible for food spoilage (André et al., 2017).

The Arrhenius (1889) law was presented in a paper quantifying a chemical reaction:

$$k_{(T)} = Ae^{-\frac{E_a}{RT_K}}. \quad (1)$$

This equation describes the linear relationship between the logarithm of the inactivation rate k and the reciprocal of the temperature (T_K) expressed in Kelvin, where A is the frequency factor (also called pre-exponential factor), E_a is the activation energy, and R is the ideal gas constant. This model is commonly used to quantify the impact of temperature on chemical reaction rates.

The Arrhenius equation was then used successfully to quantify the impact of temperature on the rate of inactivation of microorganisms. Eq. (1) can be reparametrized to give Eq. (2). The activation energy E_a quantifies the heat sensitivity of microorganisms.

$$\text{Ln } k = \text{Ln } k^* - \frac{E_a}{R}\left(\frac{1}{T_K} - \frac{1}{T_K^*}\right). \quad (2)$$

In 1921, Bigelow observed a linear relationship between temperature increase and logarithm of heat treatment time to achieve the same reduction in the microbial population (Bigelow, 1921).

In 1923, Ball modeled this relation (Eq. (3)), quantifying the heat sensitivity by the parameter z, which is the increase in temperature reducing the heating time by a factor of 10 (Ball, 1923).

$$\log D = \log D^* - \frac{T - T^*}{z}. \quad (3)$$

Concerning the kinetics of inactivation, in 1943 Katzin et al. quantified the heat resistance by the parameter D, which is the decimal reduction time (Katzin et al., 1943). In 2002, Mafart and collaborators quantified the heat resistance of bacteria when the inactivation kinetics is not of order 1. The Weibull model was re-parameterized using the

* Corresponding author.
E-mail address: sandre@ctcpa.org (S. André).

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Nomenclature

N0	initial concentration of cells (CFU mL^{-1})
N	concentration of surviving cells after the heating time t (CFU mL^{-1})
D	decimal reduction time of surviving spores or cells from N to N/10 (min)
δ	Weibull model scale parameter: first decimal reduction time of surviving spores or cells from N0 to N0/10 (min)
δ*	estimated δ value corresponding to T* (min)
p	Weibull model shape parameter
k	inactivation rate (min^{-1})
k*	inactivation rate at the arbitrary reference T* (min^{-1})
T	heating (°C) temperature
T_K	heating temperature (K)
T*	arbitrary reference temperature (°C)
T_{K*}	arbitrary reference temperature (K)
z_T	temperature increase which leads to a ten-fold reduction in δ value. z_T quantifies the dependence of the bacterial spore thermal sensitivity on temperature (K or °C)
E_a	activation energy (kJ mol^{-1})
R	ideal gas constant. (8.314 10^{-3} kJ mol^{-1} K^{-1})

slope parameter δ, corresponding to the first decimal reduction time, and the shape parameter p. The primary kinetic model can then be written as:

$$\log\frac{N}{N_0} = -\left(\frac{t}{\delta}\right)^p. \quad (4)$$

The parameters of the kinetics of inactivation k and δ can be linked.

$$Ln\frac{N}{N_0} = -kt = -(Ln(10))\left(\frac{t}{\delta}\right)^p \quad (5)$$

$$k = \frac{(Ln(10))t^{p-1}}{\delta^p} \quad (6)$$

When t = delta, Eq. (6) can be reduced into k = Ln 10/delta which becomes independent of p. For the first decimal reduction time, D equals δ and the parameters of the kinetics of inactivation can be linked. The correspondence between δ and k then becomes:

$$k = \frac{Ln(10)}{\delta} = \frac{Ln(10)}{D}. \quad (7)$$

Both models (Arrhenius and Bigelow) yield very close estimations of k or D despite their apparent incompatibility: both are exponential laws, but the input variable of one is temperature, while the input variable of the other one is temperature reciprocal. These two approaches, Arrhenius and Bigelow, have been used simultaneously. The Arrhenius approach is widely used by chemists in chemical engineering, while the Bigelow approach is more often by microbiologists in food process engineering.

Both models are conventionally connected (Eq. (8)), allowing parameter z to be defined knowing the activation energy and vice versa:

$$z = \frac{Ln(10) \times R \times T_K \times T_K^*}{E_a}. \quad (8)$$

To simplify the calculations, an approximation is used by taking $T_K \times T_K^* = T_K^{*2}$ for sterilization temperatures close to 121.1 °C (394.1 K). But this approximation leads to a divergence when the temperatures T_K and T_{K*} move apart.

The goodness of fit of the two models has seldom been compared over a wide range of temperatures. One main reason is the difficulty in obtaining heat resistance over a wide range of temperature, since the D or δ values are difficult to measure if they are below a few seconds or above a few hours. As far as we know, only four publications have z-values obtained with 5 to 7 D-values using heating temperatures spanning a range of 30 °C (Bender and Marquis, 1985; Rodrigo et al., 1997; Palop et al., 1999a; Palop et al., 1999b; Xu et al., 2006). Xu et al. (2006) used both models, but without comparing the heat resistance of *Bacillus anthracis* obtained with the two different equations. To obtain very low D-values with *Bacillus subtilis*, Palop et al. (1999b) used a thermoresistometer TR-SC, a former version of the thermoresistometer Mastia, which allows z-values to be estimated over a wide range of temperatures.

The aim of this research was to compare Arrhenius and Bigelow models over a wide range of temperatures. Thermal inactivation of bacterial spores was performed on four types of spore-forming bacteria. The spores are both mesophilic and thermophilic, belonging to aerobic and anaerobic species. The heat resistance was measured over a wide range of temperatures with two types of techniques (capillary tube and thermoresistometer) to allow comparison of the two heat resistance models.

2. Materials and methods

2.1. Biological material

Four species were selected as representing different genera of spore-forming bacteria encountered in canned food: mesophilic or thermophilic and aerobic or anaerobic bacteria. Strains were isolated from spoiled canned foods during CTCPA (Centre Technique pour la Conservation des Produits Agricoles) studies or obtained from international collections (Table 1).

2.2. Spore suspensions and heating temperature ranges

The spore suspensions were prepared according to the French Standard Method NF T 72–231 (Afnor, 1998) as summarized below. First, the cell suspensions after incubation at 37 °C for mesophilic species or 55 °C for thermophilic species in brain heart infusion (Biokar Diagnostics, Beauvais, France) for aerobic strains and Rosenow broth (Biorad, Villeneuve-d'Asq, France) for anaerobic strains were inoculated onto sporulation agar media. Aerobic bacteria sporulation medium consisted of 10 g/L beef extract, 2 g/L yeast extract, 0.04 g/L $MnSO_4{\cdot}H_2O$, and 15 g/L agar. The anaerobic bacteria sporulation medium consisted of 30 g/L tryptone, 5 g/L glucose, 20 g/L yeast

Table 1
Origin of studied strains associated to temperature range tested.

Specie	Strain	Growth condition	Origin	Temperature range tested (°C)
Bacillus coagulans	3105 018	Mesophilic and aerobic	Spoiled canned duck liver	90.0–125.0
Clostridium sporogenes	PA 3679	Mesophilic and anaerobic	ATCC	87.5–112.5
	3222 002		Spoiled canned sardines	
Geobacillus stearothermophilus	2804 081	Thermophilic and aerobic	Spoiled canned mushrooms	97.5–137.5
	2804 138		Spoiled canned greens beans	
Moorella thermoacetica	1901 042	Thermophilic and anaerobic	Spoiled canned dairy drink	115.0–137.5

extract, 1 g/L sodium thioglycolate, and 15 g/L agar. Incubation was performed at either 37 or 55 °C depending on the species, and for 2–5 days for aerobic species and 3–4 weeks for anaerobic species. The anaerobic incubation are performed in a jar. For anaerobic species 90% of spores was observed by microscopy, they were harvested by flooding the agar surface with sterile water and transferring into a sterile centrifugation tube. The spore suspension was centrifuged at 4000 ×*g* for 20 min at 4 °C, and the pellet was washed three times following the same protocol, re-suspended in 20 mL of sterile distilled water, heat-treated (80 °C for 10 min for mesophilic species or 100 °C for 10 min for thermophilic species), and then stored for one month at 4 °C before analysis. The suspension concentration exhibited up to 10^8 spores/mL. To determine the concentration of spores, the French standard NF V 08–602 was used (Afnor, 2011) as described below. The aerobic spores were counted by pouring 1 mL on Bromocresol Purple Agar (Biokar Diagnostics, Beauvais, France). The mesophilic *B. coagulans* was incubated at 37 °C, and thermophilic *G. stearothermophilus* at 55 °C, both for 48 h. The anaerobic spores were counted by pouring 1 mL on meat-liver glucose agar (Biokar Diagnostics, Beauvais, France) complemented with 2 g/L yeast extract. The mesophilic *C. sporogenes* was incubated for 48 h at 37 °C, and the thermophilic *M. thermoacetica* for 5 days at 55 °C under anaerobic conditions.

2.3. Heat treatment of spore suspensions

To ensure the widest range of heating temperatures for each species, two methods of determining heat resistance were used. For the lowest heating temperatures, heat resistance was determined using capillary tubes, and for the highest temperatures, where fast inactivation was obtained, a thermoresistometer Mastia was used. For both methods, spore suspensions were suspended in 0.2 M phosphate buffer pH 7. Heating treatments were performed at temperatures ranging from 87.5 °C to 137.5 °C and times ranging from 56 h to 2 s for extreme values. Capillary tubes (Ringcaps®Duran®) containing 100 µL of spore

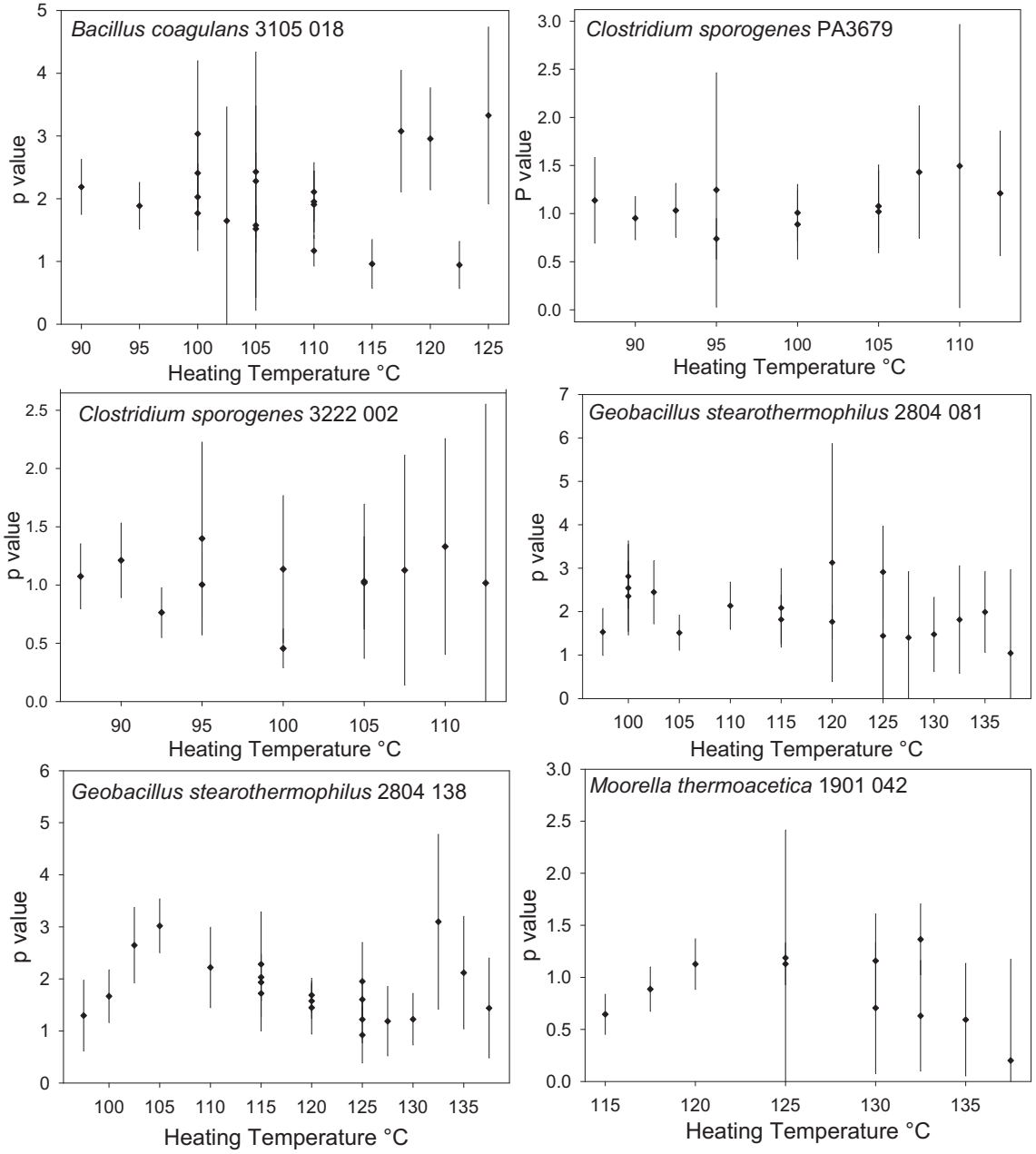

Fig. 1. *p* values fitted independently on each inactivation kinetic versus heating temperature for spores of six bacterial strains.

suspensions were heated in an oil bath. Immediately after treatment, samples were cooled in iced water. With the thermoresistometer Mastia, spores were inoculated in buffer pre-stabilized at the treatment temperature, and samples were taken at preset sampling times and cooled (Conesa et al., 2009). After cooling, the suspension was flushed out with sterile tryptone-salt broth, and the surviving bacteria able to form colonies were counted in agar media as described above.

2.4. Data analysis

Inactivation kinetics were described by the Weibull primary model (Eq. (5)). For each studied bacterial strain, the scale parameter values were determined for each temperature with a single p shape parameter value (Couvert et al., 2005). From Fig. 1 it can be checked that no relationship appears between p values and heating temperature, p and δ values were determined independently on each kinetic for the different bacterial strain studied. So, a single p value was fitted on a set of kinetics for each bacterial strain studied (Mafart et al., 2002). To homogenize the data for Arrhenius and Bigelow equation fitting, the parameter k, the inactivation rate used in the Arrhenius model, was calculated from the values of the corresponding Weibull parameters δ for time corresponding to the first decimal inactivation time using Eq. (7).

The heat sensitivity parameters E_a and z were determined for each species by fitting the Arrhenius (Eq. (3)) and Bigelow (Eq. (4)) models parameters values to the k values and δ values, respectively.

The primary and secondary model parameter values were estimated by minimizing the Sum of Squared Errors of the model on MATLAB (fmincon, Optimization Toolbox; MATLAB 7.9.0; MathWorks, Natick, USA). Their confidence intervals (CI) at 95% were estimated with the nlparci function (Optimization Toolbox; MATLAB 7.9.0; MathWorks, Natick, USA).

3. Results and discussion

For each of the strains studied, the heat resistances quantified by the scale parameters δ associated with a single slope parameter p are presented in Table 2. For the anaerobic strains *Moorella thermoacetica* and *Clostridium sporogenes* the p value was close to 1, so the kinetics of inactivation are almost log linear. For the aerobic strains, *Geobacillus*

Table 2
Weibull model parameters with their associated confidence interval estimated for different strains and heating temperature studied.

	Bacillu coagulans 3105 018		*Clostridium sporogenes* PA 3679		*Clostridium sporogenes* 3222 002		*Geobacillus stearothermophilus* 2804 081		*Geobacillus stearothermophilus* 2804 138		*Moorella thermoacetica* 1091 042	
	p	CI	p	CI	p	CI	p	CI	p	CI	p	CI
	1.83	± 0.15	0.99	± 0.10	0.91	± 0.12	1.99	± 0.18	1.82	± 0.13	1	± 0.11
T (°C)	δ (min)	CI	δ (min)	CI	δ (min)	CI	δ (min)	CI	δ (min)	CI	δ (min)	CI
87.5			247.8*	± 60.4	291.5*	± 75.2						
90.0	728.2*	± 67.4	88.39*	± 19.32	98.76*	± 27.73						
92.5			67.62*	± 16.47	75.26*	± 21.07						
95.0	107.1*	± 10.2	23.82*	± 5.74	24.82*	± 6.79						
95.0			22	± 7.93	23.82	± 7.75						
97.5							1275*	± 141	1224 *	± 138		
100.0	24.27*	± 2.66	3.77*	± 0.93	8.60*	± 2.40	866.5*	± 100.2	621.6*	± 60.9		
100.0	26.32*	± 2.80	5.19	± 1.20	7.44	± 2.65	785.3*	± 80.6				
100.0	23.32	± 2.32					825.1*	± 86.6				
100.0	26.36	± 3.50					699.4*	± 70.8	566.4*	± 53.9		
102.5	8.66*	± 1.12										
105.0	4.53*	± 0.60	0.68*	± 0.18	1.177*	± 0.36	401.8	± 42.0	234.8*	± 19.3		
105.0	6.53*	± 0.68	0.67	± 0.17	1.107	± 0.38						
105.0	8.06	± 1.08										
105.0	7.1	± 1.22										
107.5			0.34	± 0.08	0.37	± 0.19						
110.0	2.04*	± 0.21	0.15	± 0.06	0.14	± 0.06	90.83*	± 9.29	67.1	± 7.03		
110.0	1.59*	± 0.17										
110.0	1.51	± 0.15										
110.0	1.6	± 0.16										
112.5			0.05	± 0.01	0.06	± 0.04						
115.0	0.63	± 0.07					23.28*	± 2.29	15.30*	± 1.30	208.1*	± 42.43
115.0							40.21	± 4.36	14.61*	± 1.23		
115.0									31.54	± 3.82		
115.0									29.8	± 3.33		
117.5	0.18	± 0.02									140.9*	± 28.02
120.0	0.07	± 0.01					5.51*	± 0.53	3.26*	± 0.30	57.86*	± 11.58
120.0							11.99	± 2.36	2.95*	± 0.27		
120.0									4.55	± 0.46		
122.5	0.06	± 0.01										
125.0	0.04	± 0.01					1.39*	± 0.14	0.66*	± 0.07	14.86*	± 2.93
125.0							1.83	± 0.29	0.82*	± 0.07	12.64	± 5.06
125.0									1.58	± 0.15		
125.0									1.53	0.17		
125.0												
127.5							0.73	± 0.15	0.46	± 0.06		
130.0									0.34	± 0.03	3.81*	± 0.72
130.0							0.44	± 0.06			3.94	± 0.99
132.5									0.17	± 0.02	1.35*	± 0.28
132.5							0.2	± 0.03			1.11	± 0.25
135.0							0.09	± 0.01	0.06	± 0.01	0.23	± 0.05
137.5							0.04	± 0.01	0.02	± 0.00	0.16	± 0.05

stearothermophilus and *Bacillus coagulans*, the *p* value ranged from 1.8 to 2, which corresponds to concave inactivation kinetics (Figs. 1 and 2).

To compare the impact of the methodology on the heat resistance, the δ values were determined with the two methodologies (capillary and thermoresistometer) for three temperatures (Fig. 2). For *M. thermoacetica*, *C. sporogenes* and *B. coagulans* strains, the δ values and their associated confidence intervals show that there are no significant differences whatever the method used (Table 2). For the two strains of *G. stearothermophilus* studied, the heat resistance appears twice higher in the thermoresistometer than in the capillaries. However, Rodrigo et al. (1997) have determine $D_{121°C}$ value on other strain of *G. stearothermophilus* in distilled water and mushroom extract using the two inactivation methods. No significant difference has been observed. Moreover, these differences do not affect the fitting of the secondary models. Data from two inactivation methods are used without restriction for all secondary model and not effect of method can be observed in Fig. 2 when logδ is plotted versus heating temperature, even for *G. stearothermophilus*.

The heat sensitivity parameters E_a and z associated with their confidence intervals and the coefficients of determination R^2 are presented in Table 3 for the strains under study, together with some other data obtained from the literature. The values of the heat sensitivity parameters z between 6.82 °C and 8.49 °C obtained in this research are within the values given in the literature, though in the lower range. The heat resistances of anaerobic species studied appear to be more dependent on temperature increase than the aerobic species, i.e., lower z values.

Regarding the application of the Arrhenius and Bigelow models, the coefficients of determination of 0.974 to 0.995 and Fig. 3 show the high fit quality of the two models over the temperature ranges studied. We note that the two models give an identical quality of fit for the six strains studied. The figures show the linearity of the experimental data for the two models for all temperature ranges and for the six strains, and the differences between the coefficients of determination for Bigelow and Arrhenius fit are from 0.004 to −0.002.

Our experimental data show that the two techniques used to determine the heat resistance of microorganisms are equivalent. This can also be observed from the results presented by Rodrigo et al. (1997) and Fernandez et al. (1994). Thermal treatments of spores of *G. stearothermophilus* ATCC12980 were carried out in distilled water at 121.1 °C using two methods. The value of $D_{121°C}$ obtained by the capillary method (1.77 min) are close to that obtained by the thermoresistometer (1.59 min).

The goodness of fit for the Arrhenius and Bigelow models on the heat resistance values obtained in this study for a wide temperature ranges is in line with other previous studies. Some authors have

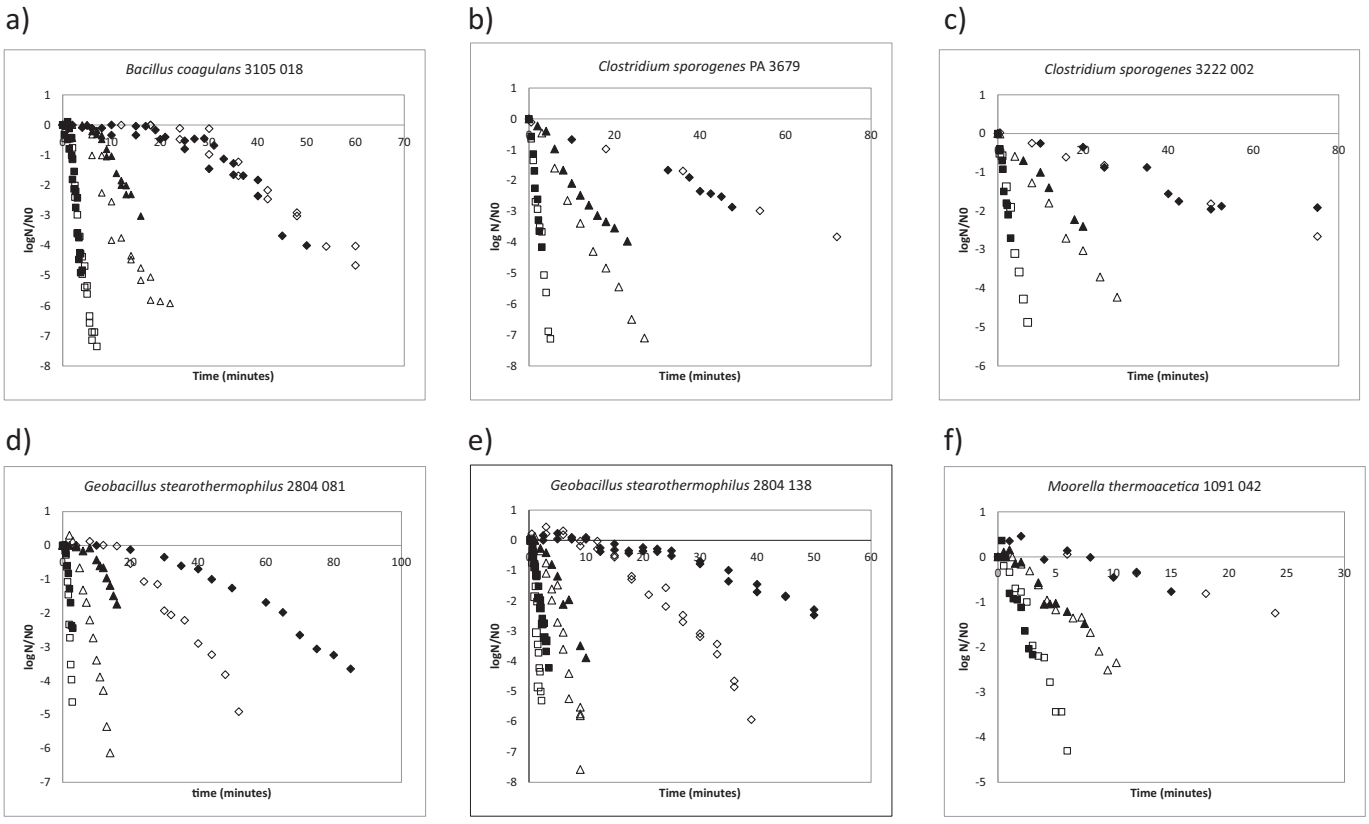

Fig. 2. a: Log N vs heating time for *Bacillus coagulans* 3105 018, at 100 °C ◊, 105 °C Δ and 110 °C □, heat treated in capillary tube (empty symbol) or in thermoresistometer (full symbol).
b: Log N vs heating time for *Clostridium sporogenes* PA 3679, at 95 °C ◊, 100 °C Δ and 105 °C □, heat treated in capillary tube (empty symbol) or in thermoresistometer (full symbol).
c: Log N vs heating time for *Clostridium sporogenes* 3222 002, at 95 °C ◊, 100 °C Δ and 105 °C □, heat treated in capillary tube (empty symbol) or in thermoresistometer (full symbol).
d: Log N vs heating time for *Geobacillus stearothermophilus* 2804 081, at 115 °C ◊, 120 °C Δ and 125 °C □, heat treated in capillary tube (empty symbol) or in thermoresistometer (full symbol).
e: Log N vs heating time for *Geobacillus stearothermophilus* 2804 138, at 115 °C ◊, 120 °C Δ and 125 °C □, heat treated in capillary tube (empty symbol) or in thermoresistometer (full symbol).
f: Log N vs heating time for *Moorella thermoacetica* 1091 042, at 125 °C ◊, 130 °C Δ and 135 °C □, heat treated in capillary tube (empty symbol) or in thermoresistometer (full symbol).

Table 3
z and E_a parameter values associated with their determination coefficients R^2 estimated on large temperature ranges.

Species and strains	Heating media	References	Data number	T (°C) range	z (°C)	R^2	Ea (kJ·mol^{-1})	R^2
Bacillus coagulans 3105 018	0.2 M phosphate buffer pH 7	This study	20	35.0	8.36	0.995	333.2	0.991
Clostridium sporogenes PA 3679	0.2 M phosphate buffer pH 7	This study	12	25.0	6.82	0.997	389.7	0.995
Clostridium sporogenes 3222 002	0.2 M phosphate buffer pH 7	This study	12	25.0	6.87	0.989	386.6	0.986
Geobacillus stearothermophilus 2804 081	0.2 M phosphate buffer pH 7	This study	18	40.0	8.36	0.989	328.1	0.987
Geobacillus stearothermophilus 2804 138	0.2 M phosphate buffer pH 7	This study	21	40.0	8.49	0.987	342.0	0.983
Moorella thermoacetica 1091 042	0.2 M phosphate buffer pH 7	This study	11	22.5	7.12	0.977	427.0	0.974
Bacillus anthracis 7702	Whole milk	Xu et al., 2006	5	40.0	9.36	0.996	270.3	0.998
Bacillus anthracis ANR-1	Whole milk	Xu et al., 2006	5	40.0	8.43	0.981	300.0	0.986
Geobacillus stearothermophilus ATCC12980	Double distilled water	Rodrigo et al., 1997	8	25.0	8.68	0.986	419.6	0.987
Geobacillus stearothermophilus ATCC12980	Natural mushroom	Rodrigo et al., 1997	7	22.0	7.27	0.994	407.3	0.993
Geobacillus stearothermophilus ATCC12980	Mushroom pH 6.2	Rodrigo et al., 1997	8	25.0	8.06	0.991	407.3	0.992
Geobacillus stearothermophilus ATCC12980	Mushroom pH 5.3	Rodrigo et al., 1997	8	25.0	9.42	0.989	319.2	0.990
Bacillus coagulans NTCC4522	Tomato pH 4	Palop et al., 1999a	5	20.9	12.8	1.000	228.4	0.998
Bacillus coagulans NTCC4522	Tomato pH 7	Palop et al., 1999a	5	20.9	8.92	0.960	322.6	0.956
Bacillus coagulans NTCC4522	Asparagus pH 4	Palop et al., 1999a	6	27.6	11.29	0.996	255.2	0.995
Bacillus coagulans NTCC4522	Asparagus pH 7	Palop et al., 1999a	8	24.1	8.76	0.995	337.2	0.997
Bacillus subtilis STCC4524 native 32 °C	McIlvaine buffer (pH 7)	Palop et al., 1999b	9	30.0	8.58	0.996	326.6	0.995
Bacillus subtilis STCC4524 native 52 °C	McIlvaine buffer (pH 7)	Palop et al., 1999b	9	35.0	8.68	0.997	327.9	0.996
Bacillus subtilis STCC4524 demineralized 32 °C	McIlvaine buffer (pH 7)	Palop et al., 1999b	8	22.0	7.27	0.995	380.6	0.993
Bacillus subtilis STCC4524 demineralized 52 °C	McIlvaine buffer (pH 7)	Palop et al., 1999b	7	20.0	7.05	0.999	394.5	0.998

determined the heat resistance of bacterial spores over temperature ranges of 20 °C to 40 °C. Different species were studied: *B. anthracis* (over a range of 40 °C) by Xu et al., 2006; *B. coagulans* (over a range of 21 °C or 28 °C) by Palop et al., 1999a; *B. subtilis* (over a range of 20 °C or 35 °C) by Palop et al., 1999b, and *G. stearothermophilus* (over a range of 22 °C or 25 °C) by Rodrigo et al., 1997.

On the 16 data sets resulting from these studies, the coefficients of determination show good linearity between log D and temperature for the Bigelow model and between ln k and $1/T$(K) for the Arrhenius model. The coefficients of determination R^2 given for fitting parameters for the two models were 1.000 to 0.956, and greater than 0.990 for 26 adjustments. For our results and those of the authors mentioned above, the comparison of the differences between the determination coefficients corresponding to the model of Bigelow and Arrhenius parameter fitting (−0.004 to 0.005), show that the fits of the two models are equally good.

While early work successfully used the Arrhenius equation for fitting the logarithm of the inactivation rate as a function of heating temperature (Madsen and Nyman, 1907). As early as 1910, Chick observed a linear relationship between the inactivation rate logarithm and temperature, but when attempting to compare this relationship with the Arrhenius equation she could not find any difference in goodness of fit. Despite the apparent incompatibility of the two models, even within a wide range of heating temperatures, they yield the same goodness of fit. This prompts a comparative mathematical analysis of the two equations (Chick, 1910).

To homogenize the form of these models, Eqs. (3) and (4) need two transformations. First the D value can be calculated from k values (Eq. (7)).

Secondly, the decimal logarithmic form has to be transformed into Neperian form. Eq. (3) can then be written:

$$\mathrm{Ln}\, k = \mathrm{Ln}\,(\mathrm{Ln}\,(10)) - \mathrm{Ln}\left(\frac{\mathrm{Ln}\,(10)}{k^*}\right) + \frac{\mathrm{Ln}\,(10)}{z}(T_K - T_K{}^*). \tag{9}$$

Arrhenius and Bigelow equations will yield the same values provided that:

$$\mathrm{Ln}\, k^* - \frac{E_a}{R}\left(\frac{1}{T_K} - \frac{1}{T_K{}^*}\right) = \mathrm{Ln}\,(\mathrm{Ln}\,(10)) - \mathrm{Ln}\left(\frac{\mathrm{Ln}\,(10)}{k^*}\right) + \frac{\mathrm{Ln}\,(10)}{z}(T_K - T_K{}^*). \tag{10}$$

This equation can be simplified and rearranged into the following form:

$$\frac{E_a}{RT_K} + \frac{\mathrm{Ln}\,(10)}{z}T_K = \frac{E_a}{RT_K{}^*} + \frac{\mathrm{Ln}\,(10)}{z}T_K{}^*. \tag{11}$$

Eq. (10) may be rewritten more compactly:

$$\frac{a}{T_K} + bT_K = c \tag{12}$$

where $a = \frac{E_a}{R}$, $b = \frac{\mathrm{Ln}\,(10)}{z}$ and $c = \frac{E_a}{RT_K{}^*} + \frac{\mathrm{Ln}\,(10)}{z}T_K{}^*$.

From Eq. (11), it can be seen that theoretically, Arrhenius and Bigelow relationships can yield the same values only at the reference temperature. The two values should diverge as the heating temperature differs from the reference temperature. However, if the first term of Eq. (12) remains practically constant for a given micro-organism over a wide range of temperatures, then inactivation rate values calculated from the two models should be very close.

Before analyzing the behavior of the c factor, two remarks can immediately be made. Firstly, retaining as a reference temperature 120 °C (393 K), and adding (or subtracting) 20 K to (or from) this temperature, the variation of c should be only 5.1%. Secondly, it can be seen, from the left side of Eq. (13), that as temperature increases, a decrease in the first term will roughly balance out by an increase in the second term.

When the heating temperature is different from the reference temperature, the expression of c is as follows:

$$c = \frac{E_a}{RT_K} + \frac{\mathrm{Ln}\,(10)}{z}T_K. \tag{13}$$

Then

$$\frac{dc}{dT_K} = -\frac{E_a}{RT_K{}^2} + \frac{\mathrm{Ln}(10)}{z}. \tag{14}$$

When $\frac{dc}{dT_K} = 0$, the c value has a minimum at the following particular temperature:

$$T_K{}^0 = \sqrt{\frac{E_a z}{R\mathrm{Ln}\,(10)}}, \tag{15}$$

and

$$c_{\min} = \frac{E_a}{RT_K{}^0} + \frac{\mathrm{Ln}\,(10)}{z}T_K{}^0. \tag{16}$$

If the chosen reference temperature is $T^* = T^\circ$, at $c = c_{\min}$, then the two models are mathematically strictly equivalent. At what interval from $c_{\min}$ will they significantly diverge? Let us arbitrarily take as a validity borderline a c increase of 1% ($c = 1.01\ c_{\min}$). The range of temperature within which the c variation is less than 1% can be

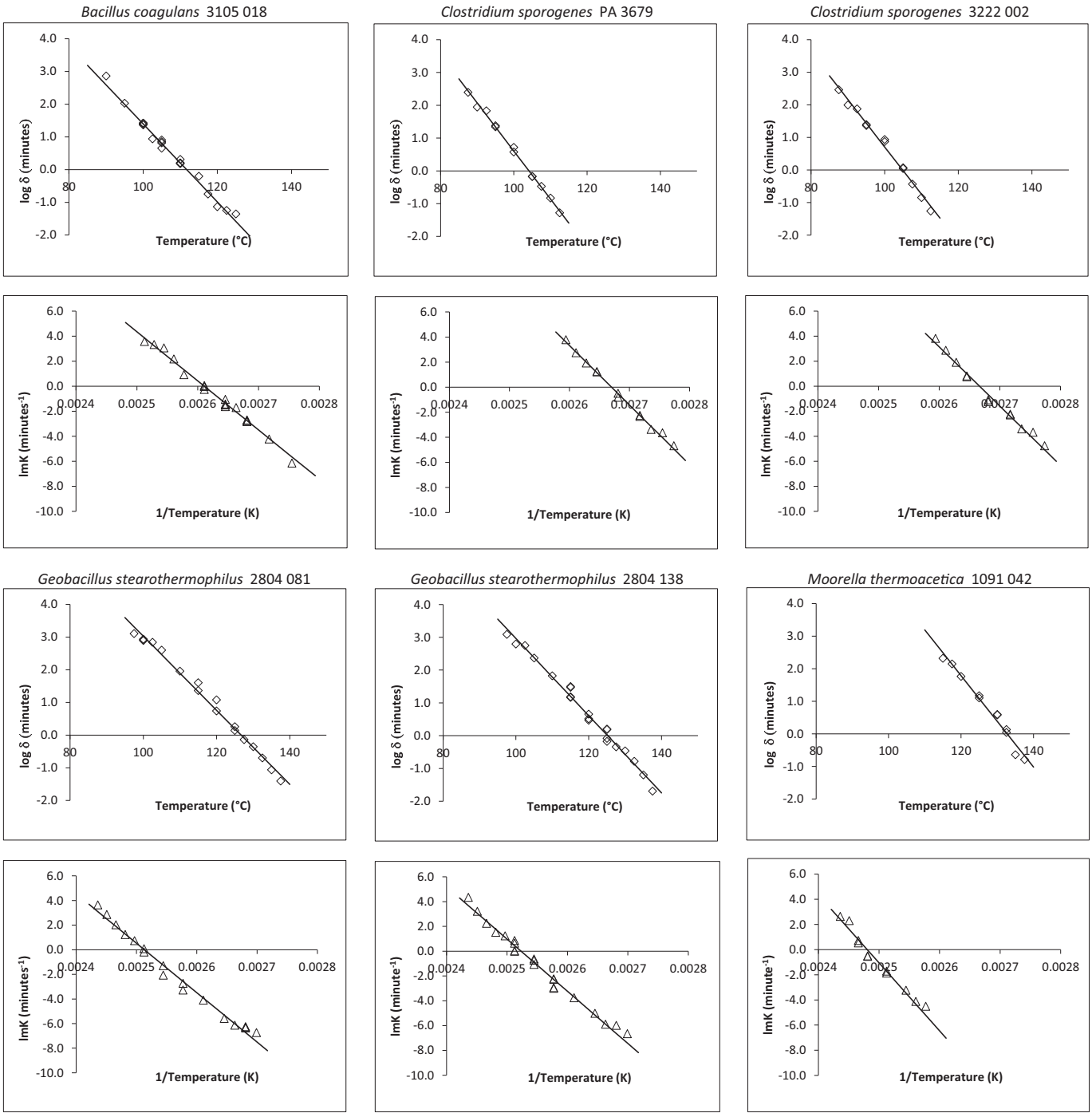

Fig. 3. Relationships logδ vs temperature (°C) and lnK vs 1/temperature (K).

calculated from:

$$1.01c_{\min} = \frac{E_a}{RT_K} + \frac{\mathrm{Ln}\ (10)}{z} T_K. \tag{17}$$

This can be rearranged into:

$$\frac{\mathrm{Ln}\ (10)}{z} {T_K}^2 - 1.01c_{\min} T_K + \frac{E_a}{R} = 0. \tag{18}$$

The roots of Eq. (18) correspond respectively to the lowest and the highest temperature that mark the bounds of the temperature range within which Arrhenius and Bigelow equations yield practically the same inactivation rate values:

$$T_{k\,\mathrm{inf}} = z \frac{1.01c_{\min} - \sqrt{(1.01c_{\min})^2 - \frac{4E_a \mathrm{Ln}\ (10)}{zR}}}{2\mathrm{Ln}\ 10}, \tag{19}$$

and

$$T_{k\,\mathrm{sup}} = z \frac{1.01c_{\min} + \sqrt{(1.01c_{\min})^2 - \frac{4E_a \mathrm{Ln}\ (10)}{zR}}}{2\mathrm{Ln}\ 10}. \tag{20}$$

It can be seen from Table 4, that these temperature ranges are quite wide, more than a hundred degrees. This explains why in the heating sterilization temperature range used, no significant difference is observed between the goodness of fit of Arrhenius and Bigelow models on heat resistance parameters.

Table 4
Central temperature of experimental data set and calculated lower and the higher temperature limits (Eqs. (19) and (20)) where Arrhenius and Bigelow equations yield give 1% deviation of inactivation rate deviation.

Species	Strain	Lower temperature (°C)	Central temperature (°C)	Higher temperature (°C)
Bacillus coagulans	3105 018	58.1	108.4	166.4
Clostridium sporogenes	PA 3679	50.5	99.6	156.2
	3222 002	50.4	99.6	156.3
Geobacillus	2804 081	64.4	115.9	175.2
stearothermophilus	2804 138	64.8	116.3	175.7
Moorella thermoacetica	1901-042	73.2	125.5	185.6

4. Conclusion

Despite the apparent mathematical incompatibility of the two equations, it is recognized that they yield the same goodness of fit. This paper finds a mathematical reason for this convergence. The difference between these two approaches is related more to their field of use. For food process optimization such as sterilization, pasteurization or cooking, the Bigelow concept is mainly used. This preference can be explained by the more concrete significance of the parameters z and D relative to the parameters E_a and k. The Arrhenius model is preferred for quantifying chemical reactions and is used to quantify the heat sensitivities of entities such as enzymes or vitamins. We note that its connotation is mistakenly mechanistic, whereas it is a simple fitting equation. To optimize pasteurization and sterilization processes associating bacteria and enzyme inactivation with vitamin conservation, Bigelow's approach is generally preferred.

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