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Received for review December 28, 1984. Accepted December 16, 1985.

Estimating Thermal Degradation in Processing of Foods

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Breakdown of heat-labile constituents in foods is approximated as a first-order chemical reaction, mathematically similar to the destruction of bacteria. Experimental time/temperature histories of several processes were each transformed into a single degradation value with known or assumed temperature–response (z) values. With this simple procedure, processes and processing steps that were major contributors to thermal degradation of desirable attributes could be identified and modified to minimize loss of quality. Examples are given to illustrate the procedure and some of its applications.

INTRODUCTION

Thermal processing is one method by which fresh foods, limited in both time and space, are preserved and made available out of season or remote from growing areas. The purposes of processing are to destroy pathogenic and/or spoilage-causing microorganisms, to inactivate natural heat-labile toxins and enzyme systems that cause degradation in the food, and to achieve a desirable texture. However, while thermal destruction of the detrimental elements is occurring, nutrients and other desirable attributes are being simultaneously destroyed at varying rates (Ball and Olson, 1957; Stumbo, 1973). The rate of destruction depends primarily upon the susceptibility of the microorganisms, enzymes, or nutrients to degradation by heat. In general, the susceptibility of microorganisms to thermal destruction is much greater than that of enzymes or nutrients. This difference in susceptibility, combined with the heating characteristics of foods, has led to the development of a variety of thermal processing methods, all of which aim at optimizing the preservation of foods.

This paper is not a basic study of the reactions that take place when food is exposed to heat. Rather, it is a practical look at the exposure of food to heat during processing, to identify the types of degradation and the places where they occur. It is an attempt to quantify degradation by a method that can be applied for optimizing processes for a particular food product or can serve as a tool in evaluating the application of heat and the resulting thermal degradation in existing processing systems. Admittedly, the procedure is crude for the sake of simplicity and general usability, but it points out differences between processing methods and highlights the steps in a process where undesired thermal degradation and waste of energy occur.

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THEORY

Consider a heat-labile constituent. It may be a vitamin, or color, or an enzyme, etc. Upon heating, this constituent changes or breaks down into products that are stable under the given conditions.

$$\underset{\text{heat-labile constituent}}{A} \longrightarrow \underset{\text{heat-stable substances}}{\text{PRODUCTS}} \quad (1)$$

The first approximation is to treat this breakdown as a first-order chemical reaction (Alberty and Daniels, 1979), and the rate of disappearance of the labile constituent can be expressed as

$$-dC_A/dt = kC_A \quad (2)$$

$-dC_A/dt$ is the rate, the change in concentration of the constituent (dC_A) in a time interval (dt), and k is the reaction rate constant.

Equation 2 may also be expressed by using the D value concept, where D' is analogous to the D value commonly used in thermal process calculations to characterize microbial destruction rates:

$$d \log C_A/dt = -1/D' \quad (3)$$

$D' = 2.3/k$ is analogous to the decimal (90%) reduction value in the thermal destruction of bacteria. D' is a function of temperature, approximated empirically by

$$D'_T = D'_{T_{ref}} 10^{(T_{ref}-T)/z'} \quad (4)$$

0021-8561/86/1434-0392$01.50/0

Obviously, D'_T is an exponential function of temperature (T) relative to a reference temperature (T_{ref}) and the corresponding $D'_{T_{ref}}$ value characteristic of a constituent in question. The z' value is a constant, analogous to the z value of the thermal destruction of bacteria, and characteristic for each chemical reaction of a particular constituent involved in thermal degradation.

During heat processing, microorganisms are destroyed progressively and more rapidly as the temperature rises in the container. Thus, the value of thermal destruction imparted during processing can be integrated over the time, by the following equation:

$$\text{sterilizing value} = F_{T_{ref}}{}^{z} = D_{T_{ref}}(\log a - \log b) = \int_0^{t_b} dt/10^{(T_{ref}-T)/z} \quad (5)$$

where a = original concentration of microorganism, b = concentration at time t_b (same units as a), $D_{T_{ref}}$ = D value for the organism at reference temperature (T_{ref}), and z = a value that characterizes the organism's response to change in temperature (Leonard et al., 1975a). Similarly, by substituting values characteristic of a heat-labile constituent into eq 5, we can integrate and obtain a thermal degradation value for the process. This value will be a "cooking" value at T_{ref} and can be designated as

$$C_{T_{ref}}{}^{z'} = D'_{T_{ref}}(\log a' - \log b') = \int_0^{t_b} dt/10^{(T_{ref}-T)/z'} \quad (6)$$

The term ($\log a' - \log b'$) represents the magnitude of change in the concentration of the heat-labile constituent through processing time t_b. By multiplying this value by $D'_{T_{ref}}$ we define the cooking value, i.e., equivalent heating (cooking) time in minutes at constant temperature T_{ref}. Analogous to the F value, the C value represents the total effect of heating on a heat-labile constituent and can be determined by evaluating the integral. The integral involves both time and temperature of the operation and the z', which is characteristic of the specific reaction. For many reactions of interest in food processing, z' is approximately 33.2 °C (59.8 °F), which is calculated from Q_{10} = 2 (Evenden and Marsh, 1948; Feliciotti and Esselen, 1957; Schanderl et al., 1962; Leonard et al., 1964). The Q_{10} value represents a change in reaction rate with 10 °C (18 °F) change in reaction temperature. Q_{10} relates to z' as follows:

$$z'\,(°C) = 10\ °C/\log Q_{10} \quad (7)$$

In most examples, Q_{10} = 2 and T_{ref} = 100 °C (212 °F) will be used with the reference cooking value $C_{100}{}^{33.2}$ ($C_{212}{}^{59.8}$) designated as C_0 (Leonard et al., 1964).

For a constant-temperature process, the integral in eq 6 is simply

$$C_0 = 10^{(T-100)/33.2} \times \text{time} \quad (8)$$

That is, C_0 is simply the exponential function of temperature (T) relative to a reference temperature, multiplied by the processing time. For processes with several steps at constant temperatures in a series, the C_0 value is the sum of the $(C_0)_T$ values at various temperatures in the individual steps of the process.

$$C_0 = (C_0)_{T_1} + (C_0)_{T_2} + (C_0)_{T_3} + \ldots \quad (9)$$

ASSESSMENT OF THERMAL DEGRADATION

To illustrate this procedure for evaluation of thermal degradation, three examples with different products are given:

Example 1. Thiamin Loss in Canned Tuna. Tuna chunks processed by two methods were evaluated for both sterilizing and thermal degradation values of the process and the actual percent retentions of thiamin (Seet et al., 1983). One of the processes involved cooking the canned product 120 min at 115.6 °C in a still retort; the other employed a high-temperature/short-time (HTST) sterilization procedure with continuous agitation (Heil, 1983). Thiamin retention was determined experimentally by assaying tuna samples before and after processing (AOAC, 1975). The results are summarized in Table I. The HTST process imparted a 30% higher sterilization (F_0) value to the canned tuna, while causing only a fraction of the thermal degradation that the tuna received in the still retort process.

Table I. Consequences of Thermal Processes for Canned Chunks of Tuna in 303 × 406 Cans (Heil, 1983)

	still retort	HTST with contin agitation
sterilizing value ($F_{121.1°C}{}^{10°C}$), min	25	33
thermal degradation value ($C_{121.1°C}{}^{25°C}$), min	123	39
retention of thiamin (AOAC, 1975), %	16.0 ± 2.0	55.8 ± 14.8

Table II. Consequences of Thermal Processes for Canned Whole Peeled Tomatoes (Leonard et al., 1975a,b)

	rotary pressure cooker	HTST with contin agitation
sterilizing value ($F_{100}{}^{15}$), min	36.0	36.8
thermal degradation value ($C_{100}{}^{33.2}$), min	38.5	13.6
ascorbic acid, mg/100 g	11.82 ± 1.02	15.83 ± 0.90
texture (shear press reading)	0.94 ± 0.35	1.36 ± 0.16

Values for the kinetic parameters for thiamin destruction, z' = 25 °C and $D'_{121.1°C}$ = 154 min, are well documented in the literature (Feliciotti and Esselen, 1957; Jen et al., 1971). Because the z' value is known, C values may be obtained from eq 10 by integrating the time/temperature history of the process.

$$C_{T_{ref}}{}^{z'} = \int_0^{t_b} dt/10^{(T_{ref}-T)/z'} \quad (10)$$

And because the D' value is known, percent retention can be calculated from the C value by eq 11, thereby saving both the time and expense of bench-top analytical procedures.

$$C_{T_{ref}}{}^{z'} = D'_{T_{ref}}(\log a' - \log b') \quad (11)$$

For the still retort process, the result of eq 10 was $C_{121.1}{}^{25}$ = 123 min. From eq 11 with $D_{121.1}$ = 154 min, a = 100%, and $C_{121.1}{}^{25}$ = 123 min, the value of b' at the end of the retort process was calculated to be 15.9%. This percent retention for thiamin is within the range of the analytical results of 16.0 ± 2% shown in Table I. Similarly, for the HTST process, $C_{121.1}{}^{25}$ = 39 min resulted in a calculated b' = 55.8% retention, which is in complete agreement with the analytically determined 55.8 ± 14.8%.

Example 2. Ascorbic Acid and Texture Changes in Canned Whole Peeled Tomatoes. In the second example for in-container processing, the assumption of Q_{10} = 2 was used, and thus z' = 33.2 °C. Because tomatoes can be adequately processed at 100 °C, $C_0 = C_{100}{}^{33.2}$ is the basis of evaluation. In this example, neither actual z' nor $D_{T_{ref}}$ is known for either ascorbic acid or texture. Nevertheless, C_0 values calculated from time–temperature data provide good indexes of the relative thermal degradation in the example processes (Table II). The advantages of HTST are evident again, as the HTST canned tomatoes processed at 114.4 °C (235 °F) retained significantly more ascorbic

Table III. Laboratory Scale Simulation of Aseptic Tomato Paste Line (Final Product: 26–46% Paste, Aseptic Fill)

operations	time, min	temp, °C	$C_{100}^{33.2}$, min	F_{100}^{15}, min
wash	2	21.1	0.008	
crush & steam injection hot break	2	104.4	2.726	4.000
pulper & finisher	2	93.3	1.258	0.714
cool to hold	1	37.8	0.013	
hold tank	30	37.8	0.390	
wiped film evaporator	<1	<37.8	0.013	
aseptic processing, heat, hold, cool	4	104.4	5.452	8.000
filler	<1	37.8	0.013	
total for process, min			9.873	12.714

Table IV. Pilot Plant Simulation of Good Manufacturing Practice Tomato Paste Line (Final Product: 26–46% Paste, Aseptic Fill)

operations	time, min	temp, °C	$C_{100}^{33.2}$, min	F_{100}^{15}, min
wash	10	21.1	0.040	
crush & rotary hot break	10	98.9	9.260	8.310
pulper & finisher	2	82.2	0.580	0.126
preevaporator	10	71.1	1.340	0.120
wiped film evaporator	1	37.8	0.013	
aseptic line	5	104.4	6.815	10.000
total for process, min			18.048	18.556

acid ($p < 0.01$) and better texture ($p < 0.05$) than those processed in the rotary pressure cooker at 102.2 °C (216 °F) (Leonard et al., 1975a,b) with the same sterilizing value (F_{100}^{15}). Thus, an informed choice may be made as to which process one should choose to improve the quality of the finished canned product.

Example 3. Color Loss in Tomato Paste. For the final example, six systems for the manufacturing of tomato paste were evaluated. These systems covered a range of processing severity, including the ideal conditions of a laboratory simulation of an aseptic line, pilot simulation of good manufacturing practice (GMP), and four commercial operations filling into cans or drums. Time–temperature data were collected and color changes measured.

In the laboratory simulation, the tomatoes were washed, crushed in a steam injection hot break system, run through a pulper and finisher, and cooled for holding. The juice was concentrated in a wiped film evaporator, and the paste was thermally processed and canned in an aseptic system utilizing scraped surface heat exchangers.

The time and temperature data, along with $C_{100}^{33.2}$ and F_{100}^{15} values, are tabulated with Table III. Both C_0 and F values are listed with too many significant figures, but the low numbers were included to indicate how very little thermal degradation takes place in some operations in contrast to others. For example, during the washing step, very little degradation takes place, whereas over 80% of the total degradation occurs during steam injection and aseptic processing. Steam injection was necessary to inactivate the pectic enzymes in tomatoes, and the aseptic process was necessary to destroy spores of microorganisms to sterilize the paste. The F values were calculated from eq 5 with $z = 15$ °C to represent the destruction of spores of *Bacillus coagulans* measured in tomato juice (York et al., 1975). Since the sequence of operations in the process was designed to achieve the required enzyme inactivation and sterility and was carried out under closely controlled laboratory conditions, the $C_0 = 9.87$-min degradation was concluded to be close to the minimum possible for paste production with the $F_{100}^{15} = 8$-min sterilization step used commercially.

Table V. Commercial Tomato Paste Line #1 (Final Product: 46% Paste, Frozen)

operations	time, min	temp, °C	$C_{100}^{33.2}$, min	F_{100}^{15}, min
wash (three stages)	5	32.2	0.045	
rinse	0.25	21.1	0.001	
crusher	0.1	21.1		
break	2	85.0	0.704	0.200
transfer to pulper	1	85.0	0.352	0.100
pulper & finisher	0.25	82.2	0.072	0.016
preheat to hold tank	1	90.6	0.518	0.238
hold tank	20	90.6	10.36	4.76
three-stage evaporator				
1st and 2nd	180	51.7	6.120	
3rd	0.5	90.6	0.259	0.119
surge tank	1	90.6	0.518	0.238
swept surf cooler	10	90.6–4.4	2.59	1.190
total for process, min			21.539	6.861

Table VI. Commercial Tomato Paste Line #2 (Final Product: 26% Paste in No. 10 Cans)

operations	time, min	temp, °C	$C_{100}^{33.2}$, min	F_{100}^{15}, min
wash (three stages)	5	32.2	0.045	
rinse	0.25	21.1	0.001	
cold crush	0.1	21.1		
cold break	2	68.3	0.220	0.016
transfer to pulper	1	68.3	0.110	0.008
pulper & finisher	0.25	65.6	0.022	0.001
preheat to hold tank	1	90.6	0.518	0.238
hold tank	20	90.6	10.36	4.76
three-stage evaporator				
1st and 2nd	90	51.7	3.06	
3rd	0.5	90.6	0.259	0.119
fill & close cans	0.25	90.6	0.129	0.059
rotary agitated cooker	40	90.6	20.720	9.520
cool to 125 °F	60	90.6–51.7	16.56	7.14
cool in stack	24 h	ambient	28.8	
total for process, min			80.804	21.861

Another well-controlled process, a pilot-scale simulation of good manufacturing practice, is presented in Table IV. It differed from the laboratory process in that a vertical rotary coil hotbreak tank was used to inactivate the enzymes. The pulper and finisher were larger, and a preevaporation step was included in which a volume of juice was heated under partial vacuum at 71.1 °C. Again, the thermal degradation occurred primarily during enzyme inactivation and sterilization.

In Table V, the time–temperature history of the operations involved in commercial tomato paste process #1 is presented. The final product was 46% tomato paste, filled into 208-L (55-gal) drums and frozen. When the C_0 values are observed, it is easy to locate the operations where most thermal degradation occurred. Reducing the degradation during evaporation may not be practical because it might require the replacement of costly equipment. However, reducing the holding time prior to evaporating could reduce degradation substantially. As a whole, the process is good, not very different from the pilot plant model.

In Table VI is an example of another commercial operation (#2) in which 26% tomato concentrate was canned and sterilized in No. 10 (15.7 cm × 17.8 cm) cans. Since the paste was less concentrated, evaporator time was reduced to half compared to the commercial process in Table V. However, the long sterilization and cooling offset any benefit gained in the preceding operations. Degradation imparted during the hot-fill-and-cool canning procedure could be reduced by 25% or more if the cans were water cooled to lower final temperature prior to warehousing. Aseptic canning would cause even less degradation. In Figure 1, comparison is made between this process and the

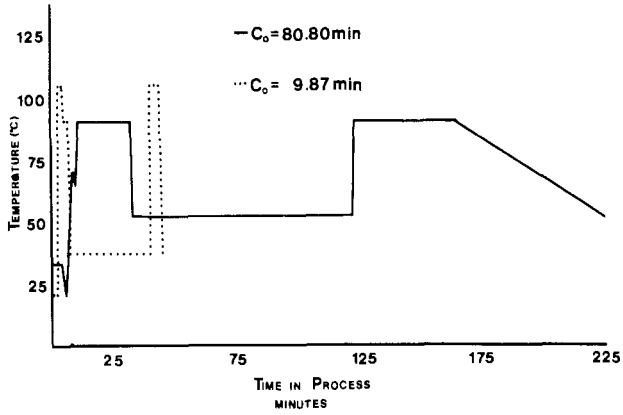

Figure 1. Comparative time–temperature histories of laboratory and commercial processes used in production of tomato concentrate. Values of corresponding thermal degradation are indicated for each process: —, commercial #2; ···, laboratory simulation.

Table VII. Commercial Tomato Paste Line #3 (Final Product: 31 °B Paste in Drums)

operations	time, min	temp, °C	$C_{100}^{33.2}$ min	F_{100}^{15}, min
wash (four stages)	10	21.1	0.040	
rotary coil hot break	10	98.9	9.260	8.130
evaporator 1st stage, three passes	45	98.9	41.670	36.570
pulper & finisher	5	93.3	3.140	1.780
hold tank (12 °B)	15	93.3	9.420	5.350
evaporator 2nd stage (22.5 °B)	45	57.8	2.385	0.045
hold tank	15	57.8	0.795	0.015
wiped film evap (28 °B)	3	96.1	2.289	1.620
hold tank	5	96.1	3.815	2.700
steam injection, flash cool (31 °B)	15	104.4	20.445	30.000
drum filler	1	37.8	0.13	
total for process, min			93.272	86.210

laboratory simulation of an aseptic line (Table III).

Data for another process (#3), which used rotary coil hot break and a two-stage evaporator, are in Table VII. About 45% of the degradation occurred in the evaporator. Since most of the process involved higher temperatures, the F_{100}^{15} value was also very high. The thermal degradation caused in the evaporating phase of the process was irreversibly high, and the resulting product did not benefit from using aseptic processing for final commercial sterilization. In fact, the sterilization step itself (steam injection, flash cool) was excessively severe.

Process #4 (Table VIII) used a two-stage evaporator system operated at lower temperatures, followed by an aseptic sterilizing/filling procedure. In this example, using high hot break and sterilization temperatures with corresponding shorter times together with minimum pulp holding times showed that improvements are possible. This process could serve as a standard of evaluation among the commercial processes.

Information supplied through the C value calculations, such as reported here, helped the respective processors streamline their procedures. The rewards were better tomato concentrate color and more efficient use of energy.

Tomato color is a major quality attribute that suffers thermal degradation (browning) from nonjudicial use of heat. Interestingly, some thermal damage measurable in terms of darker serum is beneficial to the overall red appearance of the concentrate. However, excessive heat damage can cause the concentrate to take on the brown discoloration to the point where no red would remain.

In Table IX, thermal degradation (C_0) of each process, the color of the raw material, and the color of the resulting concentrate diluted to 9° Brix are given. The C_0 values

Table VIII. Commercial Tomato Paste Line #4 (Final Product: 36% Paste in Drums)

operations	time, min	temp, °C	$D_{100}^{33.2}$, min	F_{100}^{15}, min
wash	5	20.0	0.040	
hot break	10	96.1	7.460	5.500
pulper	2	93.3	1.260	0.718
finisher	2	85.0	0.708	0.200
hold tank	13.5	85.0	4.779	1.350
evaporator				
1st stage	80	54.4	3.440	0.080
2nd stage	40	76.7	7.920	1.120
hold tank	5.5	76.7	1.089	0.154
sterilization	10	98.9	9.260	8.430
flash cool & aseptic fill	1	32.2	0.009	
total for process, min			36.145	17.552

Table IX. Comparison of Thermal Degradation of Tomato Paste Produced by Different Processes

process	final product, % solids	$C_{100}^{33.2}$, min	AG E5M color raw	AG E5M color finished[a]	grade[b]
laboratory	26–46	11	29	32	49.2
pilot plant	26–46	18	NA	NA	49.2
commercial #1	46 (frozen)	22	29	32	49.2
commercial #2	26 (No. 10 cans)	81	29	34	48.2
commercial #3	31 (drums)	93	30	39	46.2

[a] Standard dilution to 9° Brix. [b] Maximum possible grade is 50.0.

were calculated from $z' = 33.2$ °C because the actual z' value for the color change was not available and has not been determined. For an exact relationship, the $C_{100}^{z'}$ value should be calculated from the specific z' value of the constitutent being tested. In this case, the quality that is actually measured is color, and an increase of 2 points in Agtron E5M color generally resulted in a 1-point decrease in the ascribed USDA quality score. Although the 11-min increase in C_0 value from the laboratory scale samples to commercial paste #1 did not influence color, as shown by the instrument reading, a definite difference in brightness was subjectively observed by laboratory personnel. The laboratory paste appeared brighter than the commercial paste, which appeared to have deeper red color. The difference between commercial pastes #2 and #3 was dramatic. Paste #2 with $C_0 = 81$ min appeared dark red and showed acceptable color (Ag E5M = 34) whereas paste #3 with $C_0 = 90$ min (Ag E5M = 39) was both dark and brown. It appears from the data that a benefit of deeper red color derived from thermal degradation in the tomato paste up to $C_0 = 81$ min was lost by the additional heat damage between going from $C_0 = 81$ to 93 min, as confirmed by the sharp drop in USDA scores for color between the products from the two processes. Since the raw materials were not the same in these systems, a process supervisor observing these results could check to see whether tomato raw material quality or variety differences could have caused some of this difference in color. No color information was avialable for paste #4.

CONCLUSIONS

Estimating thermal degradation caused by thermal processing of foods can be accomplished from the time–temperature histories. Results will be as accurate as are the values of D' and z'. For either bulk or in-container processing of foods, the procedure can be used as a tool in choosing among processing methods or time–temperature options to optimize retentions of nutritive value and quality in the resulting product.

Processing systems, whether existing or planned, may be analyzed and easily evaluated to pinpoint operations

that contribute substantially to thermal degradation. The simple procedure is as follows: (1) Consider the temperature for each operation in a process. (2) Consider the time in each operation. (3) Calculate C_0 using $C_0 = 10^{(T-100)/33.2} \times$ time for each operation. (4) Add C_0 values from each operation to get the total C_0 value for the process. If the z' value of the specific constituent is known (or can be calculated from Q_{10}), that value should be used in place of the $z' = 33.2$ °C which is a general average value when the exact data are lacking.

Once the operations with large contributions to thermal degradation are known, alternatives for reducing the degradation in these operations become a matter of economic and practical considerations.

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Received for review December 28, 1984. Accepted June 17, 1985.

Equivalent-Point Method for Thermal Evaluation of Continuous-Flow Systems[1]

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The use of continuous thermal processing and aseptic packaging for preserving fluid foods is growing. Compared to in-can processing, continuous thermal processing offers reduced energy and packaging costs and favors product quality retention. Thermal treatments simultaneously produce beneficial and undesirable changes in products. Microbial destruction and enzyme inactivation are generally desirable, whereas quality factor changes such as with taste, color, and nutrient value are generally undesirable. Continuous thermal processes are described in terms of reaction rate kinetics. The usefulness of an equivalent-point method for optimizing the thermal treatments to achieve the desired changes with minimum undesired changes is discussed. Design criteria are examined with specific examples given.

INTRODUCTION

Continuous thermal processes associated with aseptic packaging have commonly been referred to as ultrahigh temperature (UHT). Contrary to batch heating (retorting), where exposure times can be lengthy (several minutes), UHT processes require only a few seconds. Determining the time and temperature requirement depends upon destruction of spoilage- and disease-causing microbial spores while minimizing undesirable physical, chemical, and biological transformations that occur within the product.

Desirable changes that occur during UHT processing are inactivation of biologically viable materials such as enzymes, microorganisms, and their spores. Undesirable changes are associated with loss of product quality (taste, color, nutrients, etc.). Designing for thermal optimization (maximum desirable changes and minimum undesirable changes) requires knowledge of reaction kinetics. Increased process temperature combined with decreased holding time can give the required lethal effect on microorganisms and simultaneously reduce the thermal effect on chemical reactions associated with loss of product quality, e.g. nutrient degradation. In these respects, optimization favors UHT processing.

In this paper, continuous thermal processes will be described. Process design will be discussed as it relates to reaction rate principles, and optimization of thermal treatments is examined by making use of an equivalent-point method for thermal evaluation.

CONTINUOUS-FLOW SYSTEMS

Two types of commercial continuous-flow processing systems are available: the direct and indirect heating units (Figure 1). With the indirect unit, product is heated via a heat-conducting surface, which separates the heating medium from the product. After the desired processing temperature is attained, the product is maintained at this temperature during the holding time. Cooling occurs in a separate heat exchanger, with product and cooling medium being separated again by a heat-conducting barrier. With the direct unit, product is mixed with saturated steam under pressure. This allows rapid heating of the product as the steam condenses. Again, product is held at the desired processing temperature for a given hold time.

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[1] Presented at the 187th National Meeting of the American Chemical Society in Symposium sponsored by the Agricultural and Food Chemistry Division.

0021-8561/86/1434-0396$01.50/0