

Obviously thinner or thicker strands are going to display different cooking qualities.

#### LITERATURE CITED

- American Association of Cereal Chemists, "AACC Approved Methods", 7th ed, The Association, St. Paul, Minn., 1962.
- Binnington, D. S., Johannson, H., Geddes, W. F., *Cereal Chem.* **2**, 149 (1939).
- Dahle, L. K., Muenchow, H. L., *Cereal Chem.* **45**, 464 (1968).
- Evans, G. C., deMan, J. M., Rasper, V., Voisey, P. W., *Can. Inst. Food Sci. Technol. J.* **8**, 102 (1975).
- Gilles, K. A., Sibbitt, L. D., Shuey, W. C., *Cereal Sci. Today* **11**, 322 (1966).
- Grzybowski, R. A., Donnelly, B. J., *J. Food Sci.* **42**, 1304 (1977).
- Holliger, A., *Cereal Chem.* **40**, 231 (1963).
- Holliger, A., *Buhler Diagram* **37**, 64 (1974).
- Irvine, G. N., Bradley, J. W., Martin G. C., *Cereal Chem.* **38**, 153 (1961).
- Karaesonyi, L. P., Borsos, A. C., *Cereal Chem.* **38**, 14 (1961).
- Matsuo, R. R., Irvine, G. N., *Cereal Chem.* **47**, 173 (1970).
- Sheu, R.-Y., Medcalf, D. G., Gilles, K. A., Sibbitt, L. D., *J. Sci. Food Agric.* **18**, 237 (1967).
- Voisey, P. W., Larmond, E., *Cereal Sci. Today* **18**, 126 (1973).
- Walsh, D. E., *Cereal Sci. Today* **16**, 202 (1971).
- Walsh, D. E., Ebeling, D. A., Dick, J. W., *Cereal Sci. Today* **16**, 385 (1971).
- Walsh, D. E., Gilles, K. A., *Cereal Chem.* **48**, 544 (1971).

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## Catalytic Effects of Stainless Steel, Teflon, or Glass on Thermal Degradation of Thiamin in a Tubular Laminar-Flow Reactor

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A tubular laminar-flow reactor was designed to measure the effects of contact surfaces on the kinetics of thermal degradation of thiamin. The catalytic effects of polished type 321 stainless steel, Teflon, and Pyrex glass were determined in a phosphate-citrate buffer at pH 6.60 from 70–90 °C. The rate constants were not significantly different. Thus thiamin breakdown occurred in the homogeneous liquid phase and not on the walls of the reactor.

New processing procedures and packaging materials are introduced primarily to improve quality and increase shelf life of food products. During thermal processing, fluid foods come in contact with the surface of the processing equipment at high temperatures. In storage they may remain in contact with the packaging material under reduced refrigeration for extended periods of time. These exposures could catalyze chemical deterioration of some food constituents thereby lowering quality and nutritional value. There is an urgent need for information on the catalytic effects of processing and packaging materials on the degradation of food constituents.

Pratt (1930) was among the first to study the effects of a contact surface on the stability of vitamins. He measured leaching from a nickel pasteurizer into milk and determined the effects of increased nickel content on stability of the B vitamins. However, owing to a lack of appropriate instrumentation, decisive conclusions were not made. Farrer (1947a) reported that thiamin degradation was catalyzed by iron, zinc, and nickel in a phosphate-citrate buffer, but not in a phosphate buffer. He suggested that catalysis was due to the formation of a complex between the metallic ions and citrate. Copper acted differently from the other ions, catalyzing thiamin degradation in phosphate buffer and retarding its destruction in phosphate-citrate buffer below pH 6.5. He suggested that this retarding effect was due to a complex between copper and citrate.

Factors affecting thiamin stability have been widely studied. Windheuser and Higuchi (1962) published an excellent review of the kinetics of thiamin degradation as affected by buffer salts and pH. Dwivedi and Arnold (1972) and Windheuser and Higuchi (1963) reviewed the effects of other compounds on the thermal stability of thiamin.

Thiamin degradation has been studied in the presence of several different contact surfaces and under diverse conditions. Thiamin solutions have been autoclaved in lacquer-lined cans (Morfee and Liska, 1971, 1972) and in glass vials (Dwivedi and Arnold, 1972, 1973; Dwivedi et al., 1972); sealed in glass tubes and immersed in hot water (Arnold et al., 1969; Windheuser and Higuchi, 1962, 1963; Beadle et al., 1943; McIntire and Frost, 1944); boiled and refluxed in glass systems (Booth, 1943; Farrer, 1945a,b, 1947a,b, 1948, 1953, 1955; Farrer and Morrison, 1949); and injected directly into a steam-filled stainless steel chamber (Mulley et al., 1975a,b). The different kinetic parameters reported in these studies may be attributed partly to the catalytic effects of the contact materials on thiamin degradation. Published information is lacking on effects of contact surfaces on the kinetic parameters of thiamin degradation. This study was undertaken to determine the effects of type 321 stainless steel, Teflon (FEP from Supelco, Inc., Bellefonte, Pa), and Pyrex glass on the catalyzed degradation of thiamin hydrochloride in a phosphate-citrate buffer at pH 6.60.

#### MATERIALS AND METHODS

**Apparatus.** A catalytic reactor was designed and assembled for this study (Figure 1). The electronic units, A and B, controlled the speed of the high-pressure pumps,

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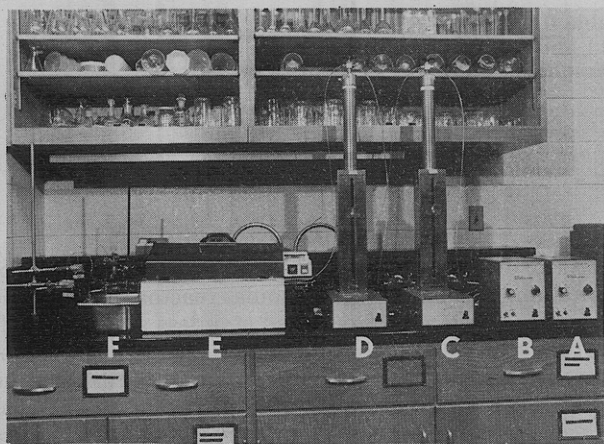


Figure 1. Laminar-flow tubular reactor. A and B, electronic units; C and D, high-pressure pumps; E, hot water bath; F, ambient temperature bath.

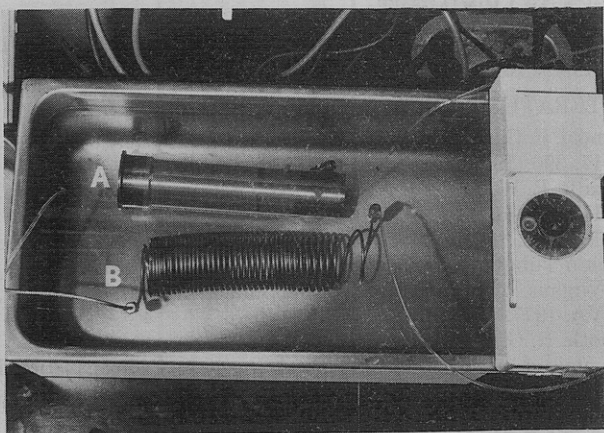


Figure 2. Two of the tubular reactors. A, Teflon coil; B, stainless steel coil.

C and D (Isco Instrument Specialties Co., Lincoln, NB). The thiamin solution was held in the reservoir of the high-pressure pump and was forced at a constant flow rate through the polished type 321 stainless steel coil, Teflon coil, or Pyrex glass coil located in the hot water bath, E. The tubing in each coil was approximately 0.32 cm o.d. The solution was cooled as it flowed through additional tubing in the ambient temperature water bath, F.

At the end of this bath, the size of the tubing for each coil was reduced by attaching 0.16 cm o.d. stainless steel tubing. This smaller tubing was then constricted sufficiently to slightly pressurize the system. The pressure prevented vapor formation at high temperatures and stabilized the flow rate.

The heat-treated thiamin sample was collected as it flowed from the constricted tube. At the end of each run, control samples were collected from the high-pressure pump reservoirs.

The electronic units, A and B, could be set at 0.8, 2, 8, 20, 80, or 200 mL/h. In a coil containing 939 cm of tubing with an i.d. of 0.213 cm (which describes the Teflon coil), residence times could range from 10 min (200 mL/h) to several days. Figure 2 shows the Teflon coil, A, and the stainless steel coil, B, inside the hot water bath. The glass coils are not shown, but were attached in the same manner. With the connection of the two coils and two pump systems, two thiamin solutions were treated simultaneously.

**Thiamin Solution and Assay.** The test solutions contained 5.0 mg of thiamin hydrochloride (I.C.N. Pharmaceuticals, Inc., Cleveland, OH) per liter of phosphate-citrate buffer (ionic strength 0.02) at pH 6.60. After

passing through the catalytic reactor, the thiamin concentration of duplicate aliquots of heated and unheated sample was determined by the procedure of the Committee on Specifications (1972) with a Turner Model 430 spectrofluorometer.

**Treatment of Data.** Results from earlier work have shown that thermal degradation of thiamin is a first-order reaction (Windheuser and Higuchi, 1962). If the thiamin concentration is represented by  $c$ , the first-order rate law can be written as

$$-dc/dt = kc \quad (1)$$

where  $k$  is the rate constant, having units of reciprocal time. If the initial concentration is  $c_0$  and if at some later time  $t_i$  the concentration has fallen to  $c_i$ , integration gives the following results

$$-\int_{c_0}^{c_i} dc/c = k \int_0^{t_i} dt \quad (2)$$

and

$$-\ln c_i/c_0 = kt_i \quad (3)$$

Thus, if one were to plot  $-\ln c_i/c_0$  vs. time, the slope would be  $k$ . This line was plotted using a least-squares linear regression.

When applied to our tubular laminar-flow reactor system, the appropriate first-order equation for the reaction and conversion in a laminar tubular reactor is

$$-\ln c_i/c_0 = (k_{i1} + S_2\kappa_{i2}'/V_1)t_i \quad (4)$$

where  $t_i$  is the residence time, and the rate constant  $k$  has been broken down into its component parts:  $k_{i1}$ , the rate constant for thiamin degradation in solution;  $k_{i2}$ , the rate constant for degradation on the tube wall;  $S_2$ , the total internal surface area of the reaction tube;  $V_1$ , the total internal volume of the tube, and  $\kappa_{i2}'$ , the equilibrium absorption constant, which is defined as the ratio of the surface concentration of thiamin on the wall to its volumetric concentration in solution. This equation assumes rapid lateral diffusion to the inner walls as compared to the rate of catalyzed surface degradation. Thus, as indicated in eq 4, the rate constant obtained in this study was a combination of the effective rate constant on the wall ( $\kappa_{i2}'k_{i2}$ ) and the rate constant in solution ( $k_{i1}$ ).

The Arrhenius temperature dependence of a rate constant can be expressed by the following equation

$$k = Ae^{-E_a/RT} \quad (5)$$

where  $A$  is the frequency factor,  $E_a$  is the activation energy,  $R$  is the gas constant, and  $T$  is the absolute temperature. This equation can be rewritten as

$$\ln k = -E_a/RT + \ln A \quad (6)$$

which can be recognized as the equation of a straight line, where  $\ln k$  is the ordinate, reciprocal temperature is the abscissa,  $-E_a/R$  is the slope, and  $\ln A$  is the intercept. This line was plotted using a least-squares linear regression program, yielding the values for  $E_a$  and  $A$ .

## RESULTS AND DISCUSSION

The rate constants for thiamin degradation and the corresponding correlation coefficients ( $r$ ) for the destruction curves are shown in Table I. As the reaction temperature increased, the rate constants increased. These rate constants are in close agreement with the results of Windheuser and Higuchi (1962) and Huttenrauch (1969). Their studies were conducted, however, in systems in which any catalytic wall effects would be less pronounced than in this reactor. At each temperature, the rate con-

Table I. Rate Constants and Correlation Coefficients for Thiamin Degradation Curves in a Phosphate-Citrate Buffer at pH 6.60

temp, °C	contact material	rate constant, min <sup>-1</sup>	correlation coefficient, <i>r</i>
70	stainless steel	1.24 × 10 <sup>-4</sup>	0.969
	teflon	1.54 × 10 <sup>-4</sup>	0.961
	glass	1.56 × 10 <sup>-4</sup>	0.998
75	stainless steel	2.20 × 10 <sup>-4</sup>	0.956
	teflon	2.96 × 10 <sup>-4</sup>	0.962
80	stainless steel	4.20 × 10 <sup>-4</sup>	0.969
	teflon	4.63 × 10 <sup>-4</sup>	0.981
	glass	4.46 × 10 <sup>-4</sup>	0.998
85	stainless steel	7.55 × 10 <sup>-4</sup>	0.973
	teflon	10.2 × 10 <sup>-4</sup>	0.988
90	stainless steel	15.3 × 10 <sup>-4</sup>	0.971
	teflon	15.0 × 10 <sup>-4</sup>	0.984
	glass	14.9 × 10 <sup>-4</sup>	0.998

stants for each of the three materials were compared using the *F* and *t* tests (Bell, 1977) and were not significantly different (*P* > 0.60). The intercepts for each of the thiamin destruction curves were statistically analyzed and none were significantly different from zero.

The correlation coefficients in Table I attest to a high level of precision for the thiamin analysis and to a high correlation between the residence time and thiamin degradation and indicate that the degradation of thiamin in this reactor was a first-order reaction. When the quantity,  $-\ln c_i/c_0$ , was plotted against time, a straight line, characterizing a first-order rate process, was observed. This is in agreement with the work of Windheuser and Higuchi (1962) and in contrast to the earlier work of McIntire and Frost (1944) and Farrer (1948).

In analyzing the reactor data, it was assumed that diffusion in the lateral direction was rapid compared to the hypothetical rate of degradation on the inner tube wall. As described elsewhere (Bell, 1977), we have mathematically tested this assumption. On the basis of the computed mass flux at the wall, the maximum concentration of thiamin in solution and the small diameter of the stainless steel tube, we concluded that no significant mass transfer limitation existed between the center of the tube and the tube walls. In essence, the maximum possible rate was far too slow to produce significant diffusion control in such a small diameter tube. Such theoretical considerations also demonstrate that this reactor is able to measure catalytic degradation effects by the inner tube walls. For much higher rates of surface degradation, a more complex theoretical analysis, patterned along the lines of the Graetz derivation (Graetz, 1885), would be required.

The energies of activation ( $E_a$ ) and frequency factors (*A*) for thiamin degradation are shown in Table II. The activation energies were calculated from rate constants which were not significantly different (*P* > 0.60). Therefore, the differences in these energies of activation cannot be considered significant. The correlation coefficients (*r*) ranged from 0.956 to 1.00. They show good reliability of the data and close adherence to the Arrhenius equation. These energies of activation agree with the data of Huttenrauch (1969).

Table II. Energies of Activation ( $E_a$ ), Frequency Factors (*A*), and Correlation Coefficients (*r*) Obtained in a Phosphate-Citrate Buffer at pH 6.60

contact material	$E_a$ , kJ/mol	<i>A</i> , min <sup>-1</sup>	<i>r</i>
stainless steel	130	6.6 × 10 <sup>15</sup>	0.996
teflon	120	2.8 × 10 <sup>14</sup>	0.956
glass	117	9.8 × 10 <sup>13</sup>	1.00

Based on the measurements for the degradation of thiamin in this laminar-flow tubular reactor, we conclude that glass, Teflon, and polished stainless steel are ineffective catalysts and that all degradation occurs homogeneously in the liquid phase. With this reactor, the catalytic effects of various materials that can be fabricated into a tube can be measured on many soluble compounds. Further work is planned to study the catalytic effects of processing and packaging materials on the thermal degradation of food constituents.

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#### LITERATURE CITED

- Arnold, R. G., Libbey, L. M., Lindsay, R. C., *J. Agric. Food Chem.* **17**, 390 (1969).
- Beadle, B. W., Greenwood, D. A., Kraybill, H. R., *J. Biol. Chem.* **149**, 339 (1943).
- Bell, J. W., "Kinetics of the Thermal Degradation of Thiamine in a Tubular Laminar-flow Catalytic Reactor," M.S. Thesis, Virginia Polytechnic Institute and State University, Blacksburg, VA, 1977.
- Booth, R. G., *Biochem. J.* **37**, 518 (1943).
- Committee on Specifications, "Food Chemicals Codex", National Academy of Sciences, Washington, DC, 1972.
- Dwivedi, B. K., Arnold, R. G., *J. Food Sci.* **37**, 886 (1972).
- Dwivedi, B. K., Arnold, R. G., *J. Agric. Food Chem.* **21**, 54 (1973).
- Dwivedi, B. K., Arnold, R. G., Libbey, L. M., *J. Food Sci.* **37**, 689 (1972).
- Farrer, K. T. H., *Biochem. J.* **39**, 128 (1945a).
- Farrer, K. T. H., *Biochem. J.* **39**, 261 (1945b).
- Farrer, K. T. H., *Biochem. J.* **41**, 162 (1947a).
- Farrer, K. T. H., *Biochem. J.* **41**, 167 (1947b).
- Farrer, K. T. H., *Br. J. Nutr.* **2**, 242 (1948).
- Farrer, K. T. H., *Austr. J. Exp. Med. Sci.* **31**, 247 (1953).
- Farrer, K. T. H., in "Advances in Food Research", Vol. VI, Mrak, E. M., Stewart, G. F., Ed., Academic Press, New York, 1955, p 257.
- Farrer, K. T. H., Morrison, P. G., *Austr. J. Exp. Med. Sci.* **27**, 517 (1949).
- Graetz, L., *Ann. Phys. U. Chem.* **25**, 337 (1885).
- Huttenrauch, H., *Pharmazie* **24**, 111 (1969).
- McIntire, F. C., Frost, D. J., *J. Am. Chem. Soc.* **66**, 1317 (1944).
- Morfee, T. D., Liska, B. J., *J. Dairy Sci.* **54**, 1082 (1971).
- Morfee, T. D., Liska, B. J., *J. Dairy Sci.* **55**, 123 (1972).
- Mulley, E. A., Stumbo, C. R., Hunting, W. M., *J. Food Sci.* **40**, 985 (1975a).
- Mulley, E. A., Stumbo, C. R., Hunting, W. M., *J. Food Sci.* **40**, 989 (1975b).
- Pratt, A. D., *J. Nutr.* **3**, 141 (1930).
- Windheuser, J. J., Higuchi, T., *J. Pharm. Sci.* **51**, 354 (1962).
- Windheuser, J. J., Higuchi, T., *J. Pharm. Sci.* **52**, 557 (1963).

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