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Edited by D. R. Heldman, Michigan State University

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MEETINGS

JUNE 1978

June 4—7: **38TH ANNUAL MEETING AND TECHNICAL AND INDUSTRIAL EXHIBIT.** Institute of Food Technologists. Dallas, Tex. C.L. Willey, Institute of Food Technologists, Suite 2120, 221 N. La-Salle St., Chicago, Ill. 60601.

June 27—30: **SUMMER MEETING OF AMERICAN SOCIETY OF AGRICULTURAL ENGINEERS.** Utah State University, Logan, Utah. Theme: Engineering Vital Resources. R.R. Kastenson, American Society of Agricultural Engineers, 2950 Niles Rd., St. Joseph, MI 49085.

JULY

July 4—7: **INDUSTRIAL WASTE TREATMENT AND UTILIZATION CONFERENCE.** University of Waterloo, Canada. E. Neil, Secretariat, University of Waterloo, Department of Chemical Engineering, Waterloo, Ontario, Canada N2L 3G1.

July 24—27: **30TH INTERNATIONAL CONFERENCE ON HANDLING PERISHABLE AGRICULTURAL COMMODITIES.** Picadilly Inn, Fresno, Calif. D.J. Florence, Conference Secretary, Assoc. of American Railroads, 59 E. Van Buren St., Chicago, Ill. 60605.

AUGUST

Aug. 13—16: **INTERNATIONAL SYMPOSIUM ON PROTEIN UTILIZATION.** Sponsored by the University of Guelph in cooperation with the Federal Ministry of Industry, Trade and Commerce. Office of Continuing Education, University of Guelph, Guelph, Ontario, Canada N1G 2W1 (519—824-4120, Ext. 3958).

SEPTEMBER

Sept. 17—22: **FIFTH INTERNATIONAL CONGRESS OF FOOD SCIENCE AND TECHNOLOGY.** Sponsored by the International Union of Food Science and Technology. Kyoto International Conference Hall, Kyoto, Japan. Secretariat, Fifth International Conference of Food Science and Technology, c/o Nippon Italy Kyoto-Kaikan, Sakyo-Ku, Kyoto 606, Japan.

FLOWABILITY OF FOOD POWDERS AND METHODS FOR ITS EVALUATION — A REVIEW

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INTRODUCTION

The term food powders represents a very wide range of powders that differ to a very great extent with regard to their chemical composition and physical characteristics (Table 1). Furthermore, the factors that effect the flowability of any given powder are numerous. They include surface properties, shape and size distribution on one hand and the geometry of the physical system on the other. It is obvious, therefore, that one general theory can hardly be applicable to all food powders and all possible conditions that may develop in practice. Furthermore, perhaps the only common feature of food powders is their tendency to develop physical and chemical changes with a strong dependency on the temperature — moisture history. As a result, a food powder should be looked upon as a dynamic system with properties that may progressively change with time.

Due to the complexity of the domain therefore, this work would only present the very general principles of powders flow and discuss their possible implication in major or common food processing and storage operations. The discussion would also be focused on those materials that are termed powders in everyday language (Table 1), and will exclude the group of granular materials (such as wheat or corn kernels). These materials have been extensively discussed by Mohsenin (1970), with a detailed reference to those pertinent aspects of powder technology. Because some of the testing procedures are based on similar principles however, effort has been made to avoid repetition as much as possible.

FLOW OF POWDERS

The mechanism involved in particulate solid flow has no similarity to liquid flow. The most remarkable practical differences are:

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Table 1. Characteristics of various food powders

Powder	Common Process of Production	Major Ingredient(s)	Commercial Moisture Content Level (%)[(a)]
Wheat flours	Milling	Starch, protein	12
Defatted soy flours	Residue of oil extraction process	Protein, carbohydrates	8
Mashed potato (flakes)	Drum drying	Starch	5
Whole milk	Spray drying	Lactose, fat, protein	2
Whole egg	Spray or freeze drying	Protein, lipids	4
Powdered onion	Grinding of dried flakes	Carbohydrates	4
Instant coffee	Spray or freeze drying (agglomeration)	Carmelized sugars, organic acids	2.6
Fruit juice drinks	Mixing	Carbohydrates (sugars) and citric acid	1
Sucrose	Crystallization and drying	Sucorse	0.5
Soup Mixes	Mixing	Salt, fat, carbohydrates	——
Ice cream & baking mixes	Mixing	Sugars, fat, carbohydrates	——

(a) Watt and Merrill (1963, 1975)

(a) In liquid flow the flow rate is proportional to the square root of the liquid head above the outlet. In powders the flow rate is independent, or almost independent, of the head provided the powder bed height is at least 2.5 times the outlet diameter, (Brown and Richards 1970).

(b) Particulate solid materials can support considerable shear stresses or form stable structures that will prevent flow despite the existing of "head".

Generally speaking, a flow of a powder is the relative movement of a bulk of particles among neighboring particles or along the container wall surface. The forces that are involved are gravitational forces, friction, cohesion (interparticle attraction) and adhesion (particle-wall attraction). The formation of a stable solid arch above the aperture is also possible. (Jenike 1967; Brown and Richards 1970).

Gravitation (pressure) is the natural driving force of unaided flow. It can also cause, however, a considerable compaction of the powder bed. Under such conditions the cohesive forces may be enhanced and the powder bed will develop "strength" with measurable mechanical properties such as tensile strength and compressive breaking strength. Flow in these terms is therefore a mechanical failure of the compacted powder bed. This led to the development of flow criteria based on solid failure theories. The most prominent theory of bulk solids flowability is the one suggested and elaborated by Jenike (1967). In food engineering textbooks, it is described by Mohsenin (1970) and by Leniger and Beverloo (1975).

Non-Cohesive Powders

Generally speaking, non-cohesive (or "free flowing") powders are those powders in which interparticle forces are negligible. It should be borne in mind though, that such forces can develop under special conditions such as moisture absorption (e.g., instant coffee), elevated temperature (e.g., fat or sugar containing powders) or static pressure (e.g., soup mixes, microcrystalline cellulose). As long as the powder is free flowing the major obstruction to flow is the internal friction. Or, in other words, the condition for flow to occur is:

$$\tau > \mu \sigma$$

where τ is the shear stress, μ the friction coefficient ($\mu = \mathrm{tg}\, \alpha$ where α the internal angle of friction) and σ is the normal stress. (See Fig. 1). Most food powders can be considered as non-cohesive only when they are dry and when their particle size is above the level of about 100 micron (White *et al.* 1967).

Cohesive Powders

As mentioned, cohesive powders are those in which interparticle forces do play a significant role in the powder bed mechanical behavior. These factors can reduce the flowability, stop it altogether or form stable bridging between particles (agglomeration). The latter phenomenon is usually referred to as a caking problem which can vary from the formation of soft lumps to the total solidification of the powder bed (Pietsch 1969). Most food powders, if unprotected, become cohesive rather easily especially due to moisture absorption.

The criteria for actual flow in any given physical system is less straightforward than in the case of non-cohesive powders. An analysis of such a system has to be more elaborated and to include both the powder properties and the geometry of the system (Jenike 1967).

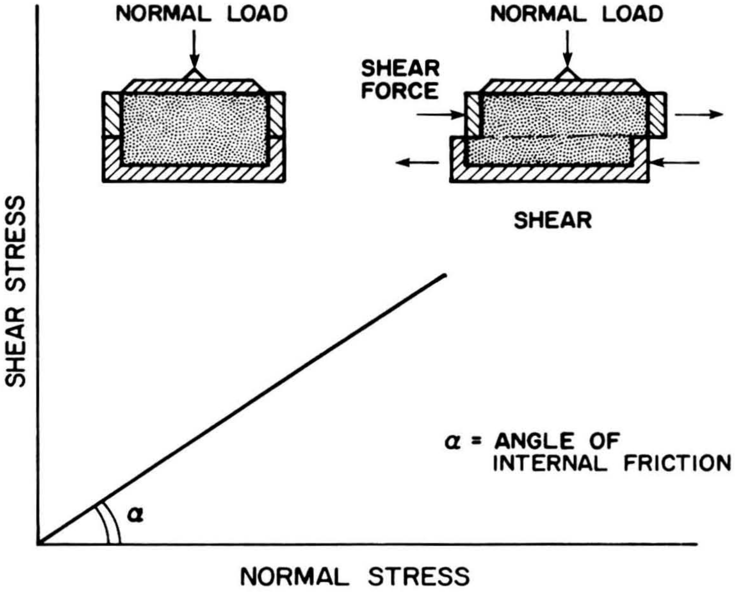

FIG. 1. THE YIELD CURVE OF NON-COHESIVE POWDER

THE NATURE OF INTERPARTICLE FORCES IN POWDER BEDS

The various kinds of mechanisms by which particles are attracted or interlocked have been classified and discussed in a classical work by Rumpf (1961) and recited by Pietsch (1969). The major mechanisms which are of concern in food powders are cited below.

Liquid Bridging

Liquid bridges can be formed when there is a liquid phase on the particle surface. This phase can be the result of:

(1) Moisture absorption (hygroscopic materials)
(2) Melting, (e.g., of fatty components)
(3) Chemical reactions that liberate liquid (e.g., browning)
(4) Excessive liquid ingredient (e.g., flavoring oils)
(5) Moisture liberation during the crystallization of amorphous sugars (Makower and Dye 1956; Berlin *et al.* 1968)
(6) Accidental wetting of the powder or the equipment.

The types of liquid bridges are shown in Fig. 2. Theoretical analysis of their contribution to mechanical strength of an agglomerate can be found in works by Rumpf (1961) and Derjagin (1961), Hotta *et al.* (1974), Schubert (1975) and Schubert *et al.* (1975).

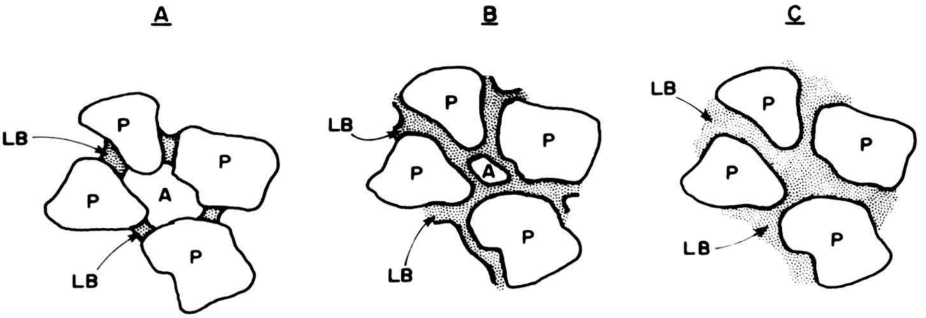

FIG. 2. SCHEMATIC REPRESENTATION OF DIFFERENT KINDS OF LIQUID BRIDGES ACCORDING TO RUMPF (1961)

P-particle LB-liquid bridge A-air. Note that any combination of the three types may also occur.

The composition of the liquid of the bridge may vary, especially in the case of food materials. This is due to the presence of numerous chemical components that have different solubilities, and different patterns by which temperature effects the latter.

The presence of the liquid bridges in itself is sometimes sufficient to obstruct flow (Peleg and Mannheim 1973) but does not necessarily result in lump formation (Makower and Dye 1959). If kept at a moderate level of moisture, for example, such a powder can maintain some degree of flowability despite the liquid bridges. If however, drying will occur after such a stage the bridges will solidify thus forming hard agglomerates or solidification of the whole bed. This process, very typical to soluble powders, (Pietsch 1969; Zimon 1969) has been termed "Humidity Caking" (Burak 1956). It has been recently discussed in connection with powdered onion (Peleg and Mannheim 1977).

Viscous liquid bridges may cause flow difficulties in fat-containing powders. The practice of cold mixing of such powders is partly due to this factor. If the temperature is elevated during processing or storage, part of the fat may melt forming liquid bridges of fatty composition. If the temperature drops later on, resolidification of the fat may occur resulting in a lumpy product. A similar problem is well recognized in the detergent industry which also uses ingredients having low melting points (Walter 1961).

A different kind of mechanism responsible for bridging is the thermoplastic characteristics of sugar-rich fruits or vegetable powders. When enough moisture is present thermoplastic properties develop at relatively low temperatures. Two examples are demonstrated:

Powder	Sticky Point[(a)] (°F)	Moisture[(b)] Content (%)	Reference
Orange juice	100	3	Notter *et al.* (1959)
	120	2	
	140	<1	
Instant sweetened applesauce (wine sap)	105	3	Lazar and Morgan (1966)
	125	0.4	

(a) The temperature of instantaneous sticking of the powder

(b) Approximated values

If after reaching the sticky point, the temperature decreases or the moisture is removed, the bridges will solidify to form hard solid bonds. Observation of this bond in polarized light reveals that they are not composed of crystals in contrast with similarly formed bonds of pure sugars (Peleg 1971).

It should also be mentioned that the formation of liquid bridges does not necessarily require the liquefaction of the whole particle mass. Local surface transformations are in most cases sufficient for bridging (Peleg and Mannheim 1973, 1977). This explains the frequent observation that caking does occur in apparently dry powders and where moisture changes are at practically undetectable levels (e.g., powdered sucrose).

Molecular Forces

Molecular attraction can be considered as a significant factor only at a short range. van der Waals forces for example have an effective range of up to about 100Å. Immobile absorbed liquid layers that can transform their excessive energy into particles attraction have similar effective range (Rumpf 1961). Possibilities of chemical interactions between the particle surfaces cannot be ruled out either. There is little information on the specific influence of such forces on the flowability of food powders. It is obvious though that their effect may become significant in very fine food powders or in compacted beds. In such cases the number of contact points between particles is considerably increased. Furthermore, because the finer the powder the larger its exposed surface area, the surface energy per unit weight (regardless of its physical-chemical character) also increases with the size reduction of the powder.

Indirect evidence of the contribution of such short-range forces in foods can be found in the work of White *et al.* (1967). They showed that various food powders did not flow when their particle size was less than 120 microns despite the fact that they were dry.

Observation by Peleg *et al.* (1973) showed that microcrystalline cellulose, a free flowing insoluble powder, could develop quite a considerable tensile strength upon exertion of relatively small pressure with very little change in bulk density. These reports, as well as the known cohesiveness of fine powders in general, cannot be regarded as a conclusive evidence for the effectiveness of short range forces at molecular levels. They do suggest or provide an indication however, that such forces may become a significant factor when fine powders are considered.

Mechanical Interlocking

Particles with irregular or fibrous shapes can be mechanically interlocked (Rumpf 1961; Mohsenin 1970). By the aid of vibration or pressure they may reach mutual orientations in which they are physically bound. The structures so formed can be mechanically stable and not always is it easy to bring the particles back to a flowing array. There is little or no evidence that such a mechanism becomes a dominant factor effecting the flowability of food powders. Under considerable pressure though a contribution by such type of mechanism cannot be ruled out.

FLOWABILITY RELATED PROPERTIES AND METHODS FOR THEIR DETERMINATION

Though the actual flowability of powder is determined by both the latter's physical properties and the geometry of the system (Jenike 1967) there are numerous experimental methods that can provide indication whether a given powder is free flowing or not. Some of these methods are discussed below.

Flow Tests

In such tests a powder is let to flow through laboratory bins or a conical funnel of different shapes. The flow can be spontaneous or aided by controlled vibrations.

In such tests, the flowability criterion is the mass flow rate. As previously mentioned, it is practically independent of the bed height if the latter is kept at a level more than 2.5 times the aperture diameter (Brown and Richards 1970). It is obvious that the method can only be applied to flowing powders. If a powder does not flow in the selected system the latter can be replaced. This, however, can be a burdensome procedure and with no guarantee that flow will eventually occur. When two or more powders do not flow under given conditions the method cannot provide clear indication on the degree of cohesiveness or suggest different conditions under which flow may perhaps be possible.

Numerous attempts have been made to correlate the mass flow rate with geometrical and physical parameters. Various such empirical equations have been cited in the literature and their application to food systems demonstrated. (Mohsenin 1970; Charm 1971; Sone 1972; Leniger and Beverloo 1975). The existence of a variety of non-coinciding equations suggests that more than a single mechanism are involved in the flow and therefore actual testing of systems is perhaps unavoidable.

From a dimensional point of view, isothermal flow through a funnel could be described as follows (White *et al.* 1969):

$$W = K\,\psi\,(\mu)\,\rho_p\,d_o^{2.5}\,g^{0.5}$$

where W is the mass flow rate K a constant, $\psi\,(\mu)$ a function of the friction coefficient ρ_p the particles density, d_o the cone apperture ($d_o >> d_{particle}$) and g the gravitational acceleration.

The limitation of this equation as well as most other empirical ones is that they cannot successfully predict conditions in which flow will stop altogether. If such equations are considered in a more restrictive way, however, they can provide useful guidelines for flow analysis, under limited conditions.

Angle of Repose

Perhaps the simplest test from a technical point of view is the measurement of the repose angle. In such a test the angle the powder forms with the horizon is determined. Regardless of the methods by which the cone (or other powder shape) is formed it can be assumed that the smaller the angle the more free flowing the powder is. As a thumb rule, powders with angle of repose of less than about 40 degress are free flowing. Powders exhibiting repose angle of 50 degrees and more are likely to cause flow problems. Because the formation of the cone involves both frictional forces, interparticle cohesive forces, and impact effects that may lead to segregation, the actual measurements depend on the experimental method procedure. It has been shown by Brown (1961) that results obtained by different techniques are significantly different and therefore incomparible.

In the case of cohesive powders irregular cones are sometimes formed and the measurement of the angle itself becomes difficult. Furthermore, powders may have different and non-uniform packing levels as well as moisture levels. Therefore, the relative contributions of the various physical factors that shape the heap may also vary with these parameters. This explains why moist powder exhibits higher repose angle (mainly due to cohesion) despite the fact that the angle of internal friction usually declines with the increase in moisture (Mohsenin 1970; Peleg and Mannheim 1973). General aspects of the repose angle have been discussed by Brown (1961), Gray (1968), Bruff and Jenike (1967, 1968), Brown and Richards (1970), and Carstensen and Chan (1976). Applications to food materials can be found in textbooks written by Mohsenin (1970). Sone (1972) and Heldman (1975).

The Principles of Cohesive Powders Characterization

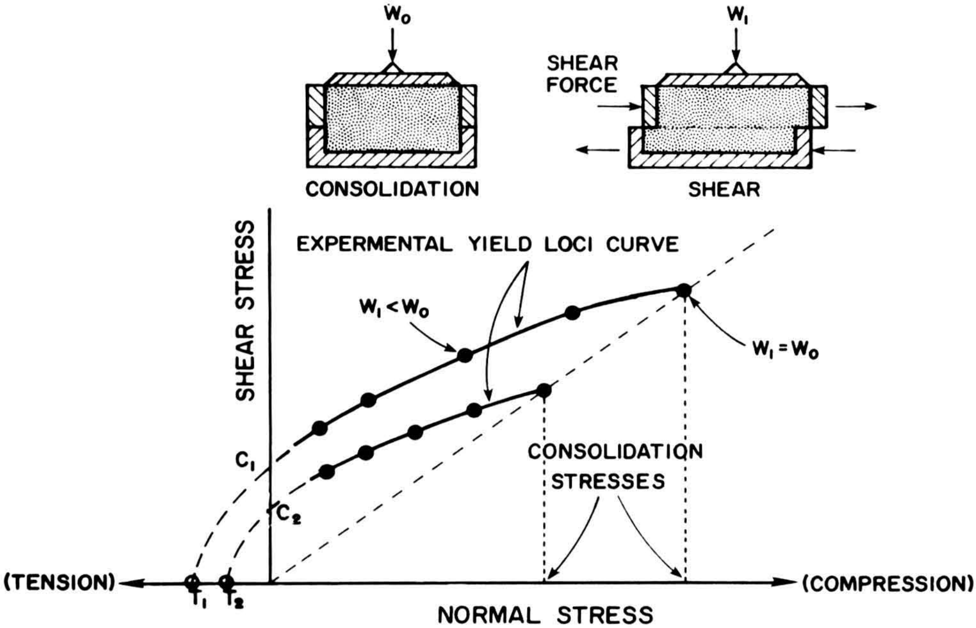

FIG. 3. THE YIELD CURVES OF COHESIVE POWDERS AT TWO CONSOLIDATION LEVELS
C_1 and C_2 — Cohesion, T_1 and T_2 — Tensile strength

A schematic view of the shear yield stress as a function of the normal stress at two consolidation levels is shown in Fig. 3. (The technical details regarding the determination of the curves are discussed later). The figure demonstrates that unlike the non-cohesive powders the cohesive powder is characterized by the following:

(a) There is a family of yield loci curves, i.e., at each consolidation level we get a different curve.
(b) The curves do not pass through the origin.

The latter indicates that at zero normal stress the compacted powder has non-zero shear strength. This parameter is referred to as "cohesion". The units of the cohesion are units of pressure and the magnitude depends not only on the powder properties but also on the consolidation conditions (C_1 and C_2 in Fig. 3).

Likewise, the yield loci curve intercepts with the normal stress axis indicate the "tensile strength" of the compact (T_1 and T_2 in Fig. 3). The values of the latter, however, cannot be calculated by mere extrapolation of the yield loci curve and various instrumental techniques have been developed for their determination.

For regular powders the yield loci at the consolidation conditions practically lie on a straight line that passes through the origin. This enables the determination of the internal angle of friction from shear tests (see below).

For a great many powders the yield loci curves can be described by the empirical equation which was suggested by Ashton *et al.* (1965) and is commonly called the Warren Spring equation:

$$\left(\frac{\tau}{c}\right)^{n} = \frac{\sigma+T}{T}$$

where τ is the shear stress, c the cohesion, σ the normal stress, T the tensile stress and n a constant which is characteristic of the powder.

Williams and Birks (1967) analyzed the energy balance when a compacted powder is sheared and arrived at the conclusion that (provided some conditions are satisfied) the cohesion is proportional to the tensile strength, or:

$$c = kT$$

where k is a constant that depends on the internal friction and the ratio between the normal and shear strains.

The practicality of their theory has been demonstrated by Farely and Valentine (1967, 1968) and Stainforth *et al.* (1970, 1971) who showed such a relationship in a variety of inorganic powders. Cheng *et al.* (1968) showed that the relationship had a strong dependency on particle size and the proportionality constant (k) in a range of up to about tenfold depending on the powder. Their measured values for soybean flour and egg powder were about k = 1.5.

Irregular Powders

In the Warren Spring equation the powder coefficient n is independent of the consolidation pressure and therefore is an intrinsic property of the tested powder. Obviously it will be affected by particle size, moisture, etc.

For some powders, however, it has been found that the assumption of a constant power coefficient n does not provide a satisfactory approximation. These powders have been termed "complex" (Kocova and Pilpel 1971, 1972) or "Irregular Powders" (Stainforth and Berry 1973). Analytical treatment of their flow behavior is significantly more difficult than that of the simple or regular powders. Another property associated with a powder "irregularity" is a static angle of internal friction that is affected by the bulk density and therefore by the consolidation pressure. Evidence for such a trend in some food powders could be found in works by Peleg *et al.* (1973). The magnitude of the shift, however, has been found to be in the order of single degrees. Generally speaking powders which become sticky upon heating or moisture absorption and show strong caking tendency also have "irregular" behavior pattern. Such materials have also been termed "complex irregular powders" (Stainforth and Berry 1975).

Measurements of Cohesion

Jenike's Flow Factor Tester. The most common instrument for flowability evaluation is the flow factor tester designed by Jenike (1967). The instrument (in its various models and modifications) provides shear force — displacement data. These can be used to plot curves of the kind shown in Fig. 3 from which the cohesion can be calculated by extrapolation. The cohesion of various food powders measured by this method is given in Table 2. Though the instrument is simple to operate and has other practical advantages it has some special aspects that need attention for the meaningful interpretation of the results. The ideal shear force-displacement curve is shown in Fig. 4A. Such surves are obtained for many dry food powders (e.g., sucrose, onion) and identifying the yield force is simple and straight-forward. In special cases a more complicated curve shape may appear (Fig. 4B). In such a case the

Table 2. Cohesion of some food powders[(a)]

Powder	Moisture Content (%)	Cohesion[(b)] (g/cm^2)
Corn starch	<11	4–6
Corn starch	18.5	13
Gelatin	~10	1
Grapefruit juice	1.8	8
Grapefruit juice	2.6	10–11
Milk	1.0	7
Milk	4.4	10
Onion	< 3	< 7
Onion	3–6	8–15
Onion	> 6	Not measurable
Soy flour	~ 8	1

(a) Data from Peleg *et al.* (1973)

(b) Determined by Jenike Flow Factor Tester at consolidation load of 6.5 kg

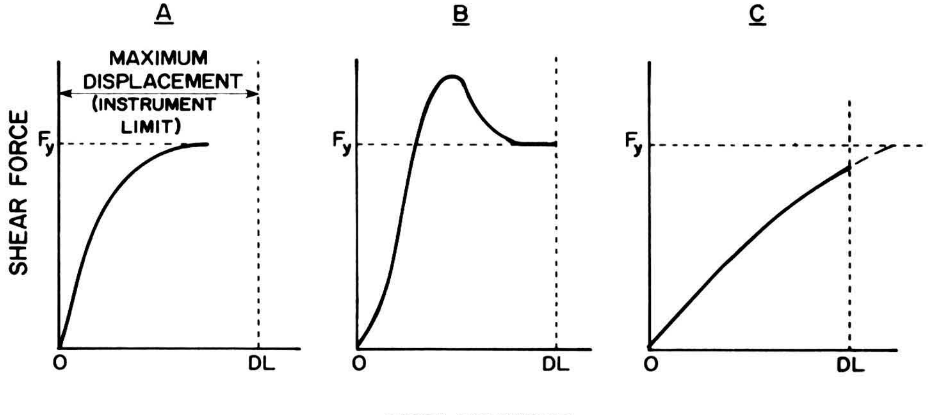

FIG. 4. TYPES OF SHEAR FORCE-DISPLACEMENT CURVES OBTAINED IN A LINEAR SHELL CELL

F_y — is the yield force. Type A curves are the basis for straightforward calculation of the flow function by Jenike's method. Types B and C require procedural or instrumental modifications — explanation in text.

experimental procedure ought to be modified. Such situations as well as other possibilities have been discussed by Williams and Birks (1965). A third shape Fig. 4C) is likely to appear in cohesive food powders (e.g., onion with more than 6% moisture, soup mix, citric acid). This kind of curve indicates that shear failure did not occur within the range of the instrument. Because the flow factor tester is based on linear motion, it has a physical limit to how much displacement is allowed.

If such a situation develops (i.e., the powder is extremely plastic and cohesive) and modification of the procedure is unlikely to improve the situation, yield data cannot be obtained. Under such circumstances, it should be mentioned, the meaning of the terms powder and flowability themselves may become questionable.

Another phenomenon that can be encountered in food powder testing is the "slip-stick effect." The latter is expressed by oscillations in the force-displacement curves (Fig. 5). The slip-stick effect is characteristic to pure starch and wheat flours. It has been suggested by Jenike (1970) that in such cases the pertinent force-displacement curve should be the one connecting the oscillation peaks as shown by the dashed curve in Fig. 5A. If such curves are the source of data to be used in design, addition of safety factors may be advisable. It is interesting to note that the admixture of calcium-stearate (a flow conditioner) introduces the slip-stick effect even if the host powder shows quite a normal shear behavior (e.g., sugars, Peleg 1971).

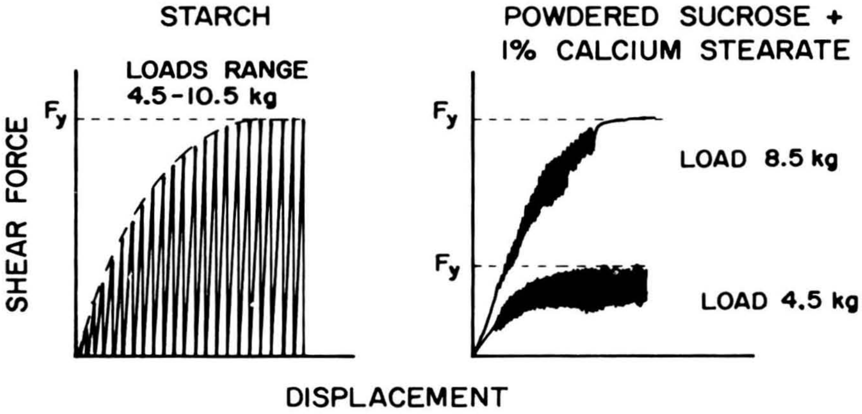

FIG. 5. SLIP-STICK EFFECT AS OBSERVED IN SOME FOOD POWDERS

Annular Cells

As mentioned the linear motion of the Jenike Flow Factor Tester or other instruments operated on same principles limits their applicability to relatively small displacements. In some cases (Fig. 4C is one example) this limitation has significant practical and theoretical implications. The latter is mainly due to the definition of the sheared area. These aspects have led to the development of annular cells in which the motion is angular. Calculation of the stresses under such conditions are less straightforward but the instruments provide at least some remedy to the deficiencies of linear instruments. Descriptions and discussions of such cells can be found in works by Carr and Walker (1967, 1968), Scarlett and Todd (1968), Kocova and Pilpel (1971) and Bagster *et al.* (1974).

Other Instruments

Though in principle similar various instrumental modification of linear and annular cell have been reported in the literature. Modifications on principle basis have also been suggested and an example is the simple shear apparatus discussed by Schwedes (1975).

Tensile Strength

The tensile strength of a powder provides a direct indication of the interparticle forces present and their magnitude. Theoretical relationships between the tensile strength and the various kinds of bonding mechanisms have been developed by Rumpf (1961). More recent in formation in this area can be found in the works of Pietsch (1969) and Schubert (1975).

Experimental procedures for tensile strength determination are generally based on measurements of the force necessary to dissect a powder compact whether directly or in a vertical or horizontal split cell. Schematic view of the different methods is given in Fig. 6. The construction aspects as well as their implications on the measurements themselves can be found in works reported by Ashton *et al.* (1964); Nash *et al.* (1965); Carr and Walker (1967, 1968); Schraemli (1967); Schubert and Schubert *et al.* (1975) and Turner *et al.* (1976).

As previously stated the measured tensile strength depends on the consolidation stress. Some typical values obtained for food powders are shown in Table 3. It should be mentioned that the classification of food powder flowability on the basis of tensile strength alone may result in erronous conclusion.

Examples are the microcellulose powder and the soup mix. Both are free flowing as long as they are not subjected to pressure and can be handled with relative ease in processing operation. (Precaution obviously ought to be taken to avoid pressure). The reversed conclusion, i.e.,

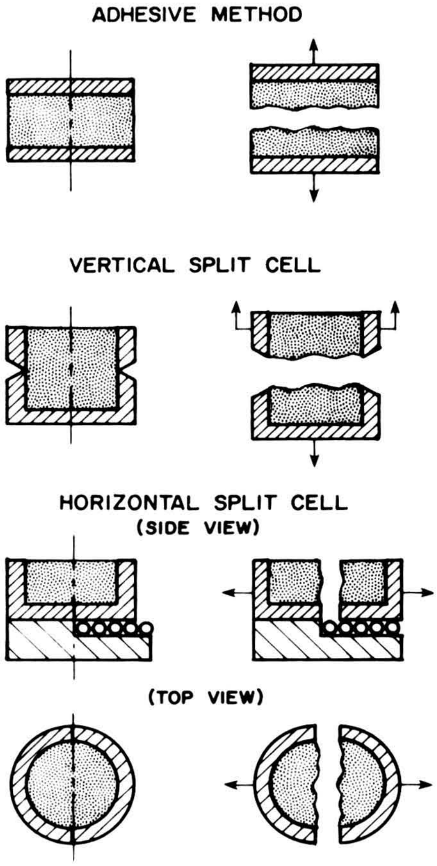

FIG. 6. SCHEMATIC REPRESENTATION OF DIFFERENT METHODS FOR TENSILE STRENGTH MEASUREMENTS

that if a powder does not develop tensile strength under pressure it is free flowing, is of course justified.

The Unconfined Yield Locus and the Flow Function

Shear analysis in terms of principal stresses and Mohr's failure criteria is currently the most commonly used tool for flowability evaluation. Practical theories and methods (like the prominent method of Jenike 1967) have been replacing the more empirical methods which are based on less fundamental characteristics of a powder system. The theoretical and practical aspects of the shear analysis have received very extensive attention in recent powder literature (Schwedes 1975; Molerus 1975;

Table 3. Tensile strength of some powders[(a)]

Powder	Moisture (%)	Tensile Strength (g/cm^2) Compacted at 0.1 kg/cm^2	Tensile Strength (g/cm^2) Compacted at 0.4 kg/cm^2
Microcrystalline cellulose	—	1.3	4
Citric acid	—	8	11
Gelatin	~9	0.015	0.04
Onion	1.0	0.1	0.13
Onion	4.5	0.3	1.5
Soup mix	—	1	8
Sucrose	dry	0.5	1
Sucrose	0.2	3	4

(a)Data determined in a vertical split cell 39 mm in diameter and 45 mm in length. The consolidation pressure was applied 25 mm above the failure plane (Peleg 1971).

Stainforth and Berry 1973) as well as in general and food engineering textbooks (Williams 1968; Brown and Richards 1970; Mohsenin 1970; Leniger and Beverloo 1975).

The basic goal of the shear analysis is to provide information about the stress a powder can support before it yields. The most convenient parameter is the unconfined yield stress which generally represents the stress level that can be supported at the compact surface. Schematic representation of the unconfined yield stress is shown in Fig. 7. The unconfined yield stress can be used as an independent measure of a powder cohesiveness (York 1975) or be used for the construction of Jenik's flow function (1967). The latter is the relationship between the unconfined yield stress (or force) and the major consolidation stress (or force) as shown in Fig. 7, and it can provide data for quantitative flowability classification as well as for construction design of silos.

Analytical methods for the calculation of flow parameters based on shear analysis have been suggested by Stainforth *et al.* (1970, 1971), Stainforth and Berry (1975), Eelkman-Rooda (1975), and Eelkman-Rooda and Haaker (1977).

Such methods enable direct calculation of the parameters with the aid of computers rather than by the old (and cumbersome) graphical methods.

Because the yield loci curves of many food materials can well be approximated by a straight line (Sone 1972; Peleg and Mannheim 1973), the flow functions could be calculated by a simple and straightforward computer program (Peleg 1971).

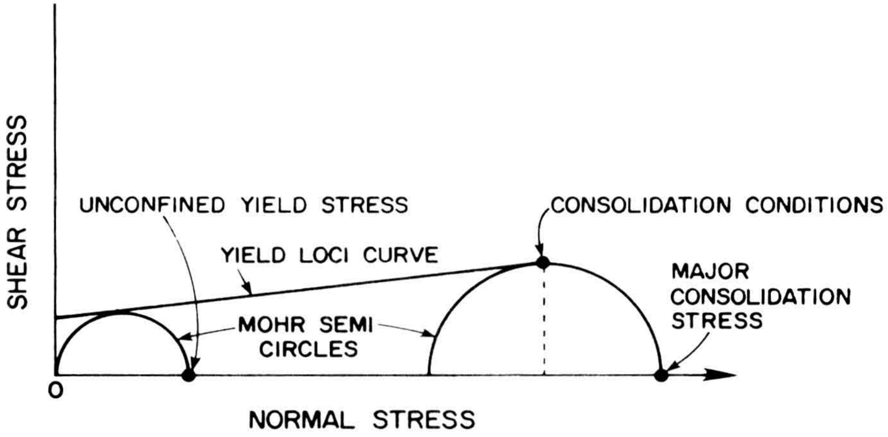

FIG. 7. CALCULATION OF PRINCIPAL STRESSES BY MOHR'S SEMICIRCLES

Angle of Internal Friction

The angle of internal friction is well-defined in non-cohesive powders (Fig. 1). For cohesive powders several different definitions have been suggested. Some of them are illustrated in Fig. 8. Discussions of the significance of the various definitions have been brought by Jenike (1967), Williams and Birks (1967), and Brown and Richards (1970). It should be mentioned again that for irregular or complex powders the angle of friction may depend on the normal stress. Some typical values of angles of frictions of food powders are given in Table 4. These show that moisture absorption drastically increased the cohesion and the tensile strength resulted in a significantly smaller angle of friction. This phenomenon can be explained by two mechanisms (Peleg 1971; Peleg and Mannheim 1973).

(a) The liquid layer that is formed on the particles surface acts as a lubricant.

(b) Solubility of parts of the particles surface smooth their shape thus eliminating rough points that promote friction.

It should also be mentioned that in cohesive food powders friction plays only a minor role in the obstruction to flow if compared to interparticle forces (Peleg *et al.* 1973).

Concentrated data on angles of frictions of food powders have been reported by Sone (1972) and Mohsenin (1970).

Bulk Density

The bulk density of a powder is primarily determined by the solid

Table 4. Angle of internal friction of various food powders determined by a Jenike Flow Factor Tester(a)

Powder	Moisture %	Angle of Friction (deg.)
Corn starch	dry	33
Corn starch	18.5	31
Grapefruit juice	1.8	38
Grapefruit juice	2.6	37
Milk	1.05	39.5
Milk	4.4	39
Sucrose (—60 + 80 mesh)	dry	39
Sucrose (—60 + 80 mesh)	52% RH	35
Analytical sand (—60 + 80 mesh)(b)	dry	40
Analytical sand (—60 + 80 mesh)(b)	1.1	36

(a) Determined at consolidation load of 6.5 kg (Peleg 1971)

(b) Part of data to support the suggestion of lubrication by liquid film. In the case of sand the water can only be present at the surface

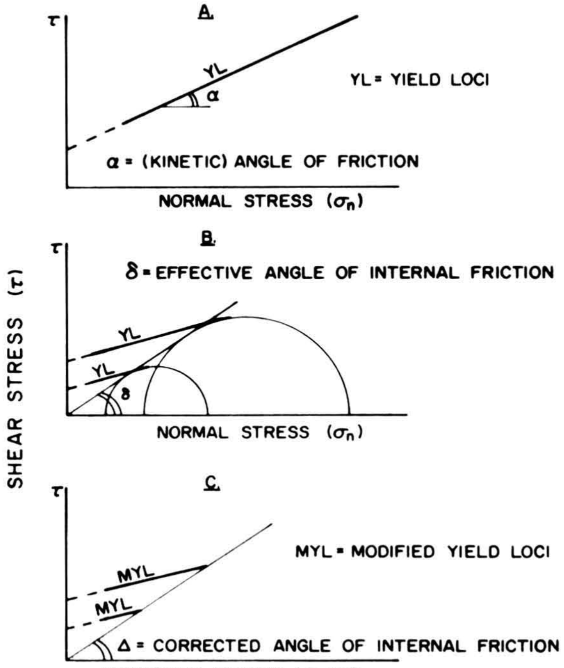

FIG. 8. VARIOUS WAYS OF REPRESENTING INTERNAL FRICTION IN POWDERS

(References and data: A. Sone 1973; B. Jenike 1967; Peleg *et al.* 1973; C. Williams and Birks 1967; Kocova and Pilpel 1973b).

density and the particles array in the bed. While the solid density is basically an intrinsic property of the material, the array which the particles form is not. The internal structure of a powder bed is influenced by a variety of factors. These include the conditions under which the bed has been formed (e.g., vibration, segregation, approach velocity), the geometry of the particles, internal friction and interparticle cohesion.

In ideal systems (e.g., metal spheres), it can be assumed that the effects of cohesion and friction are negligible in comparison with gravitational forces and therefore the possible arrays can be calculated by mathematical modeling (Gray 1968).

In cases where the particle shape is irregular and the effects of friction and cohesive forces are significant the possible arrays cannot be predicted from simplified models. Some trends, however, do exist and these have been used to evaluate or estimate the role of the internal forces. Generally speaking, a powder bed can have an open array of particles (loose packing) or a dense array (close packing). The existence or stability of the open arrays depend on the availability of mechanical forces that can support the open structure (Fig. 9). These forces may be due to friction, cohesion, particular particle shapes and any of their combinations. Because it is extremely difficult to evaluate the different contributions of these forces, it is not possible to estimate or predict the flowability of powders on the basis of bulk density alone. It can be said, however, that one of the signs that a given powder develops cohesiveness is a significant reduction in its bulk density, i.e. when freely poured into the measuring container.

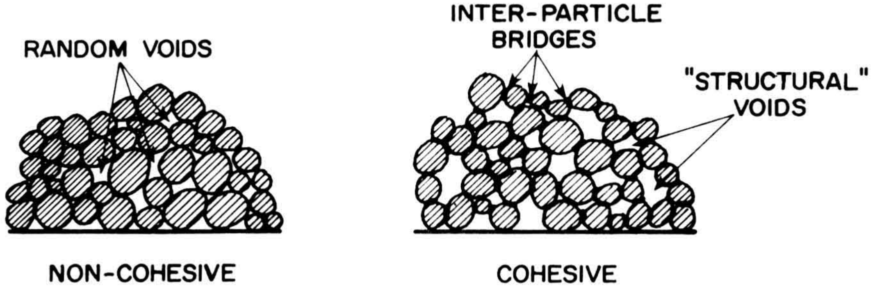

FIG. 9. SCHEMATIC VIEW OF THE PARTICLE ARRAY IN THE BEDS OF COHESIVE AND NON-COHESIVE POWDERS

Since the absolute magnitudes of both frictional and cohesive forces in the loose powder are relatively small, they can be overcome by relatively gentle means. These include vibrations or tapping and compression by application of low stresses.

Tapping

The amount of bulk density change due to tapping may be an index to the presence of attractive forces and friction. A considerable increase in bulk density due to tapping is usually interpreted as the existence of significant interparticle forces, mainly friction (Hausner 1967). The great advantage of such methods is the simplicity of the instrumentation (Sone 1972) and the test performance. It should be mentioned though that the experimental results may depend to a great extent on the test procedure (e.g. the number of taps) and such factors as particle size. Despite this limitation, however, the "Hausner Ratio," i.e. the ratio between tap and apparent bulk densities, has been found a useful criterion which well correlated with actual flowability and other physical characteristics of some powders (Grey and Bedow 1968, 1969).

Compressibility

As mentioned, the interparticle forces that enable open structure in the powder bed succumb under relatively low pressure. The term low pressure in this context refers to the range of up to about 1 kg/cm^2 in which it can be assumed that the particles themselves are not deformed or broken to a significant extent. Possible exceptions in food powders are fatty powders like soup mix and certain flours.

The general behavior of powders under compressive stresses has received great attention in powder technology. Summary and discussion of equations which describe the pressure-density (or void ratio) relationships of powders have been presented by Kawakita and Ludde (1970, 1971).

Food powders at the low pressure range generally exhibit the following relationship (Sone 1972; Peleg *et al.* 1973):

$$\mathrm{BD} = \mathrm{a} + \mathrm{b} \log \mathrm{P}$$

where BD is the bulk density, P the applied pressure, a and b constants. The constant b which in fact represents the compressibility of the powder has been found to correlate with the cohesion of a variety of food powders (Fig. 10) and therefore could be a simple parameter to indicate changes in flowability. (This was partially possible because the solid density of most food materials is around 1.6 g/cm^3).

Obviously, and as in the case of tapping, the experimental procedure is simple and does not require sophisticated or expensive instrumentation. There are, however, experimental factors that may effect the

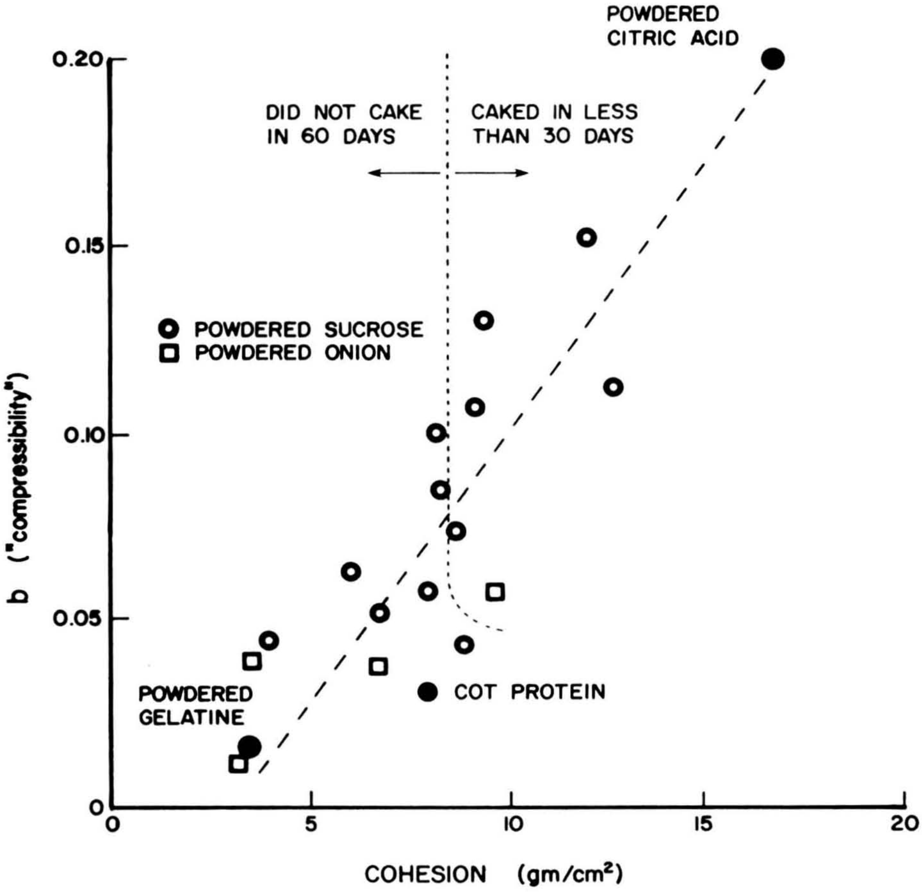

FIG. 10. COMPRESSIBILITY VS COHESION OF SOME FOOD POWDERS (DATA FROM PELEG 1971)

results (e.g., the cell dimensions, the compression time, the number of twists) and therefore the method can only provide a rough indication of flowability changes in powders.

Miscellaneous Methods

The methods that have been described are by no means the only methods to evaluate flowability. Among other techniques that have been applied to food powders is the "Rotational Viscometer". The instrument is similar in construction to viscometers used for liquids (Harwood and Pilpel 1968). The calculation of cohesion and friction, however, are done in a different way and from different testing procedures (Benarie 1961; Senna 1967). Data for food powders obtained by such methods have been published by Taneya (1963, 1965, 1969). A rotating drum has also been applied to food powders. The information in the form of the angle between the surface of the powder in the drum and the horizon was used to indicate dynamic friction (Sone 1972) or the instantaneous angle of repose (Brown and Richards 1970). The rotation speed at which free fall no longer occurred was used to indicate the degree of flowability in milk powders (Sjollema 1963).

CONCLUSIONS

The flowability of powders with reference to food powders has been briefly surveyed. The discussion revealed that there are still numerous problems which have remained unsolved. These are both theoretical and experimental in nature. The complexity of the flow phenomenon itself is intensified in the case of food powders by hygroscopicity and physical-chemical changes that have strong time dependency. In many cases (e.g. fruit juice powders) the changes are so rapid that unless special controlled environment is created all the previously described tests would become meaningless. In other specific systems, various "anomalies" can be observed (e.g., considerable particle deformation at low stresses). These can distort the meaning of experimental results which are perfectly useful in different systems.

Upon selection of a testing method, therefore, care should be taken to guarantee that the measured parameters really represent the properties we are after. This is specially important in cases where the experimental values result from a combined effect of unrelated properties (e.g., cohesion and internal friction). We should also bear in mind that actual flow depends on both the powder properties and the geometry and other physical characteristics of the system. Therefore, the term "flowability" itself has a relative meaning. In comparison to most other physical properties of foods, powder characteristics received only modest attention in the food literature. The increasing role of food powders in the food supply, both as an industrial raw material and as convenience or special finished food items would certainly change this situation. It is the belief of the author that food powder technology as active field of research would have to be developed to complement and elaborate our knowledge in this area of food engineering.

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EFFLUENT GENERATION, ENERGY USE AND COST OF BLANCHING

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ABSTRACT

Blanching and cooling of vegetables is a major source of wastewater in the vegetable processing industry. In recent years modification of conventional blancher designs have been developed.

Using material and heat balances, the theoretical effluent generation and energy use of blanching and cooling can be calculated. Actual performance of blanchers can then be compared to these theoretical quantities.

The Vibratory Blancher-Cooler, the Hot-Gas Blancher and the Hydrostatic Steam Blancher are new blancher designs that have been developed in recent years. The effluent generation and energy use of these new designs as compared to conventional steam and water blanchers can be determined from published reports.

When the operating costs of the above modifications are compared to those of a conventional water blancher, the low capital cost of the water blancher makes it the most economical choice. However, a doubling of the combined cost of energy, water and wastewater disposal would give the Vibratory Spiral Blancher-Cooler an operating cost equivalent to that of a water blancher and flume cooler.

INTRODUCTION

The wastewater produced by the blanching of vegetables for freezing or canning is a large fraction of the total wasteload of the vegetable processing industry (National Canners Assoc. 1971). Ralls and Mercer (1973) reported that, on the average, 40% of the plant BOD was due to blanching. Since the beginning of this industry, the basic design of blanchers has received little attention, but because of national concerns about wastewater and energy, changes in the design of conventional blanching systems are now being tested and evaluated.

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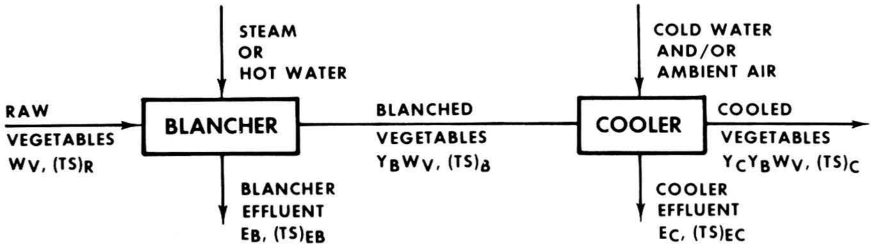
This paper describes effluent generation and energy use of conventional blanchers and new blancher designs, and it compares the cost of blanching with four different blanchers (water, Hydrostatic Steam, and Vibratory Spiral steam, and Hot Gas).

Material and Heat Balances



$$(TS)_R = Y_C Y_B (TS)_C + \underbrace{E_B \rho_B (TS)_{EB}}_{\substack{\text{BLANCHER}\\ \text{BOD}\\ \&\\ \text{SS}}} + \underbrace{E_C \rho_C (TS)_{EC}}_{\substack{\text{COOLER}\\ \text{BOD}\\ \&\\ \text{SS}}}$$

FIG. 1. MATERIAL BALANCE FOR BLANCHING AND COOLING

Figure 1 shows a material balance for blanching and cooling vegetables. Total solids of the vegetables is used as the unit for the material balance. In the effluent, Total Solids can be expressed as the equivalent Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) or Total Organic Carbon (TOC) and Suspended Solids (SS), which are all common units for measuring the organic wasteload of an effluent. In this paper the organic wasteloads of effluents will be expressed in terms of the raw vegetable; that is, kg of BOD or SS/10^3 kg of raw vegetable. The initial weight of raw vegetables changes as the vegetables are blanched and cooled because of changes in water and solids content; the yields (Y_B and Y_C) represents these changes. Reducing the wasteload of blanching and cooling translates into reducing the hydraulic load (E_B and E_C) and the organic load ($\rho_B E_B (TS)_{EB}$ and $\rho_C E_C (TS)_{EC}$) of the effluents. If air is used to cool the vegetables, then $E_C = 0$, and the cooling effluent is eliminated, but since much of the cooling is provided by evaporation of water, the yield after air cooling will be less than that after water cooling. Frozen vegetables are sold by weight, and thus the reduction in yield is a product loss. Bomben *et al.* (1975) have reported on material balances measured with seven different vegetables using either air or water cooling.

Figure 2 shows a heat balance for blanching and cooling with typical operating temperatures. Using C = 4.19 kJ/kg • °C (1 BTU/lb • °F), ΔH = 2256 kJ/kg (970 BTU/lb) and $Q_L = 0$, the theoretical steam required at 0 Pa gage pressure to heat the vegetables to an enzyme inactivation temperature can be calculated to be 134 kg of steam/10^3 • kg of raw vegetables (268 lb steam/ton raw vegetables). Note that if the only effluent from a blancher were the steam condensate produced in heating the vegetables, then the effluent would be 134 L/10^3 • kg of raw vegetable. The magnitude of Q_L determines the thermal efficiency of an actual blancher; the smaller it is, the higher the thermal efficiency. A heat balance on the cooler, using the temperatures shown in Fig. 2 and assuming that C = 4.19 kJ/kg • °C) gives 5545 L of water/10^3 • kg of raw vegetables (1320 gal/ton) for cooling vegetables in a flume (cocurrent flow) after blanching. For air cooling the heat balance is more complicated because both heat of evaporation and sensible heat are transferred. If heat were transferred solely by evaporation at $t_3 = 27$°C, then for the temperatures in Fig. 2 with C = 4.19 kJ/(kg • °C) and ΔH = 2438 kJ/kg (1048 BTU/lb):

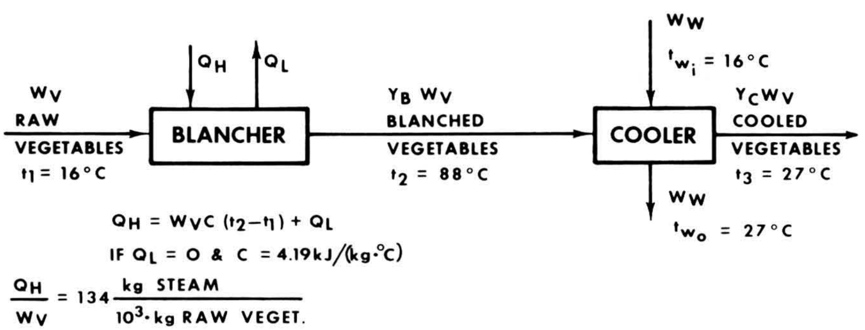


FIG. 2. HEAT BALANCE FOR BLANCHING AND COOLING

$$\frac{Wevap}{W_v} = \frac{Y_B C (t_2 - t_3)}{\Delta H} = 0.105 Y_B$$

Taking $Y_B = 95\%$ (Bomben *et al.* 1975) evaporative air cooling gives a 10% reduction in the yield of vegetables. This loss can be partially counteracted by spraying the vegetables with water or blancher condensate, but in practice the weight loss and water addition do not balance, and there is a reduction of yield and some production of effluent (Bomben *et al.* 1975).

DISCUSSION

Conventional Water and Steam Blanchers

Although conventional blanchers are different in specific design, they can be put into two basic categories — water and steam blanchers. Table 1 shows the characteristics of wastewater from conventional steam and water blanchers. The data for snap beans is for blanching prior to canning, where the temperature of snap beans is kept below 82°C, and thus the amount of effluent could be less than that theoretically calculated ($134L/10^3 \cdot kg$), where the blanching temperature was 88°C. Blanchers are operated at varying conditions, and as a result, the characteristics of the wastewater can be quite different at different times in the same plant and from plant to plant. Generally, water blanchers produce a higher hydraulic load, but their organic load is about the same as that of steam blanchers. The amount of make-up water added to a water blancher is not a well-controlled variable; Lund (1974) and Ralls and Mercer (1974) reported large variations in the measurement of effluent from water blanchers in vegetable canning plants. One plant operates a water blancher with no overflow, and it dumps the entire volume of blancher water once per week, (Perkins 1974), but since in that particular case (artichokes) citric acid is added to the blancher water, this has to be considered a special case, whose applicability to other blanched vegetables has not been investigated.

Table 1. Wasteload and energy use in conventional blanching

	Hydraulic Load $L/10^3 \cdot kg$	BOD $(kg/10^3 \cdot kg)$	SS $(kg/10^3 \cdot kg)$	Steam Efficiency (%)
Water Blanching				60
Snap Beans	124 — 334	0.69	0.13	
Lima Beans	821	0.65	—	
Peas	240 — 384	1.4 — 3.0	—	
Steam Blanching				5
Snap Beans	125 — 150	0.55	0.02	
Lima Beans	113 — 238	3.5	—	
Peas	191 — 313	4.3	—	

Data taken from Ralls and Mercer (1973), Lund (1974), and Bomben (1978).

Data on the steam consumed by conventional blanchers are very limited. Typical values are shown in Table 1, where efficiencies are based on the theoretical steam consumption of 134 kg of steam/10^3 kg of raw vegetables. Whereas the thermal efficiency for the steam blancher was a measured value (Bomben 1978), the one for the water blancher was estimated assuming that water blanchers consume less steam than steam blanchers (Lazar and Rasmussen 1964). Measurements of the actual efficiency of water blanchers were not found in the literature. The low efficiency of a steam blancher is attributable to the large losses of steam at the feed and discharge ends and the large uninsulated surface area. The thermal efficiency for the steam blancher reported here was measured on a commercially operated blancher (Bomben *et al.* 1978); however, since no other measured values were found in the literature, it is uncertain whether this value is a typical efficiency for steam blanching.

New Blancher Designs

The Vibratory Spiral Blancher-Cooler is a design which departs markedly from that of conventional steam blanchers (Bomben *et al.* 1976, 1978). Vibratory spiral conveyors are used to reduce the size of the steam blancher as compared to a water blancher, thereby reducing floor space and reducing surface area for heat loss. In addition, the spiral conveyor gives a simple means of sealing the feed and discharge of the blancher with vegetables, thereby reducing this large heat loss associated with steam blanching. In addition to the blancher, this design also uses a vibratory spiral conveyor as an air cooler, where condensate from the blancher is sprayed on the vegetables as they are cooled. Thus, the only effluent for both blanching and cooling is the unevaporated, unabsorbed liquid leaving the cooler. Table 2 shows the wasteload and the steam efficiency obtained with a pilot plant of this design (Bomben *et al.* 1976, 1978).

Table 2. Wasteload and steam efficiency of Vibratory Spiral Blancher-Cooler

	Hydraulic Load L/10^3 · kg	BOD (kg/10^3 · kg)	SS (kg/10^3 · kg)
Snap beans	27.0	0.53	0.084
Lima Beans	27.9	0.90	0.54
Brussels sprouts	15	0.43	0.073
Cauliflower	< 3		
Broccoli	11	0.25	0.091

Steam Efficiency = 85% (theoretical steam requirement = 134 kg/10^3 kg of vegetables)

Hot-Gas Blanching uses the products of combustion along with steam as a heat transfer medium (Ralls and Mercer 1974). A belt conveyor moves the vegetable through the hot gases and steam. Table 3 shows the wasteload and energy requirements obtained with a Hot-Gas Blancher pilot plant.

The Hydrostatic Steam Blancher uses water to seal the feed and discharge of a conventional steam blancher, thereby reducing the escape of steam from the blancher (Ray 1975). Some of these blanchers are operating in freezing plants, and are reported to use 0.5 kg of steam per kg of vegetable (Layhee 1975). No data are available on the wasteload produced by this system, and in this paper it is assumed that wasteload of a Hydrostatic Steam Blancher is the same as that of a conventional steam blancher and flume as reported by Bomben *et al.* (1975) and listed in Table 4.

Table 3. Wasteload and steam efficiency of hot-gas blanching

	Hydraulic Load $L/10^3 \cdot kg$	BOD $(kg/10^3 \cdot kg)$
Snap beans	0.06	<0.01
Corn-on-cob	58	0.86
Beets	93	0.63
Spinach	0.66	0.01
Peas	14	0.12

Steam efficiency = 56% (includes natural gas and electrical power for blower and is based on a theoretical steam consumption $= 134\ kg/10^3 \cdot kg$). The efficiencies of electrical and steam generation were not considered in converting electrical energy to the equivalent steam.

Table 4. Wasteload of steam blanching including water cooling

	Steam Blanching Effluent		Water Cooling Effluent	
	Hydraulic Load $(L/10^3 \cdot kg)$	BOD $(kg/10^3 \cdot kg)$	Hydraulic Load $(L/10^3 \cdot kg)$	BOD $(kg/10^3 \cdot kg)$
Snap beans	150	0.92	4930	1.6
Lima beans	113	1.1	4960	3.4
Peas	191	2.7	4960	2.9

Data taken from Bomben *et al.* (1975); Chemical Oxygen Demand was multiplied by 0.6 to get BOD.

RESULTS

Comparison of Wastewater and Energy Use

Table 5 compares the wastewater produced and the energy used for the blanching of snap beans by different methods. Wastewater characteristics are reported as hydraulic wasteload and organic wasteload (BOD and SS), and steam consumptions are reported as efficiency with respect to the theoretical value of 134 kg/10^3 • kg. In the case of Hot-Gas Blanching, the energy of the natural gas and the electrical energy of the blower as reported by Ralls and Mercer (1974) was included in the calculation of the efficiency.

Table 5. Wasteload and steam efficiency of different methods of blanching snap beans

	Hydraulic Load (L/10^3 • kg)	BOD (kg/10^3 • kg)	SS (kg/10^3 • kg)	Steam Efficiency (%)
Conventional water	124	0.69	0.13	60
Conventional steam	125	0.55	0.02	5
Hot-gas	0.06	<0.01	0.01	56
Hydrostatic steam	a	a	a	27
Vibratory spiral blancher-cooler	27	0.53	0.084	85

[a] Data for the Hydrostatic Steam Blancher were not available. In the cost estimation of this paper, it is assumed that the wasteload of a Hydrostatic Steam Blancher was the same as that of a conventional steam blancher and a water flume, as given in Table 4.

Hot-Gas Blanching produces the lowest wasteload. Its energy efficiency is an improvement over steam blanching, and it approaches that of water blanching. Despite its low wasteload, Hot-Gas Blanching is at a disadvantage because it depends on increasingly scarce clean-burning hydrocarbons.

Since its effluent is the same as a conventional steam blancher and a cooling flume, the Hydrostatic Steam Blancher makes no reduction in wasteload. Its steam efficiency is a considerable improvement over that of the conventional steam blancher, but it is less than the estimated value for a conventional water blancher.

The wasteload for the Vibratory Spiral Blancher-Cooler includes both blanching and cooling, whereas the other wasteloads shown in Table 5 do not include cooling. In preparing vegetables for freezing, flume cooling is generally used after blanching. Flume cooling, as shown in Table 4, has a larger hydraulic and organic wasteload than blanching. The Vibratory Spiral Blancher-Cooler reduces both of these wasteloads to low levels. If only the Vibratory Spiral Blancher is used, as in canning, then its wasteload would be about the same as that of conventional steam blanching. The Vibratory Spiral Blancher-Cooler has the highest steam efficiency of the blanchers shown in Table 5, thus demonstrating the effectiveness of its seals against steam leaks and its double wall insulated construction.

Cost Analysis

Table 6. Capital investment for blancher and coolers ($ as of year-end 1976)

	Vibratory Spiral Blancher-Cooler	Water Blancher	Hydrostatic Steam Blancher	Hot-Gas Blancher
Equipment purchases[1]	$108,000	$16,000	$87,000	$127,000
Delivery[2]	5,000	1,000	4,000	6,000
Installation[3]	22,000	3,000	17,000	25,000
Floor space[4]	4,000	2,000	9,000	25,000
Indirect costs[5]	35,000	6,000	30,000	46,000
	$174,000	$28,000	$147,000	$229,000

[1] Equipment purchase costs were obtained from equipment manufacturers, except for the Hot-Gas Blancher whose cost was taken from Ralls and Mercer (1974) and corrected to 1976 prices by the Marshall and Stevens Equipment Cost Index (Peters and Timmerhaus 1968). The water blancher and the Hot-Gas Blancher included an estimate of $5,000 for a cooling flume

[2] 5% of the equipment purchase cost

[3] 20% of the equipment purchase cost

[4] Floor space was valued at $270/m^2$. Floor space requirements are estimated as follows:

Vibratory Spiral Blancher-Cooler	15m^2
Water blancher	6m^2
Hydrostatic steam Blancher	33m^2
Hot-Gas Blancher	93m^2

[5] 25% of the total of items 1 to 4

Table 6 shows the capital cost of 4 blanchers. All cost data expressed here are taken as of the end of the year 1976. Since conventional steam blanchers are usually custom-fabricated, purchase costs could not be accurately obtained; therefore, it was decided not to include this type of blancher in the cost analysis. The Hydrostatic Steam Blancher can be viewed as an improved version of a conventional steam blancher, and except for a higher steam efficiency, its costs would presumably approximate those of a conventional steam blancher and flume cooler. Except for the Hot-Gas Blancher, purchase costs are based on equipment manufacturers' price quotations for a capacity of 4.5×10^3 kg/hr

(5 tons/hr) of snap beans (2.0 min blanching time). Other items in estimating direct fixed capital are taken as percentages of equipment purchase cost (Peters and Timmerhaus 1968). Floor space is valued at $\$270/m^2$ ($\$25/ft^2$). The purchase costs of the water blancher (reel type) and Hot-Gas Blancher include $5,000 for a flume cooler. The Vibratory Spiral Blancher-Cooler and the Hydrostatic Steam Blancher have the cooler as an integral part of the blancher.

Table 7. Cost of blanching and cooling for freezing ($\$/10^3 \cdot kg$)

		Vibratory Spiral Blancher-Cooler	Water Blancher	Hydrostatic Steam Blancher	Hot-Gas Blancher
			Labor Costs		
(1)	Operating Labor	0.63	0.63	0.63	0.63
(2)	Supervision, fringe benefits, laboratory, etc.	0.41	0.41	0.41	0.41
		1.04	1.04	1.04	1.04
			Capital Related Costs		
(3)	Maintenance	0.69	0.11	1.17	1.82
(4)	Depreciation	1.37	0.22	1.17	1.82
(5)	Insurance, Taxes, other expenses	1.10	0.18	0.94	1.46
		3.16	0.51	3.28	5.10
			Utilities and Waste Treatment Costs		
(6)	Steam	1.24	1.75	3.91	1.40
(7)	Electricity	0.05	0.01	0.03	0.46
(8)	Water	0.00	0.66	0.64	0.64
(9)	Wastewater	0.01	0.15	0.14	0.12
		1.30	2.57	4.72	2.62
	Total Cost	5.50	4.12	9.04	2.62

Annual production = $4.5\ 10^3$ kg/hr × 14 hr/day × 200 days/yr = $12{,}600\ 10^3$ kg/yr

(1) 1/4 man/shift for operation and 1/4 man/shift for cleaning (2 shifts/day) with average hourly wage = \$5/hr: 2 (2 + 2) × \$5/(14 × 4.5) = $\$0.63/10^3 \cdot kg$ = \$0.57/ton

(2) Supervision, fringe benefits, laboratory, supplies, etc. = 65% of operating labor

(3) Maintenance = 5% of direct fixed capital/yr for Vibratory Spiral and water blanchers and 10% of direct fixed capital for Hydrostatic Steam and Hot-gas blanchers

(4) Depreciation = 10% of direct fixed capital/yr

(5) Insurance, taxes and other fixed expenses = 8% of direct fixed capital/yr

(6) Steam = $\$7.83/10^3$ kg of steam (\$3.55/1,000 lb steam). Steam cost for Hot-Gas blancher includes cost of gas (\$0.0013/MJ) (Johnnie and Aggarwal 1977)

(7) Electricity = \$0.00389/MJ (\$0.018/kw-hr) (Johnnie and Aggarwal 1977)

(8) Water = \$0.13/kL (\$0.50/1,000 gal) (Johnnie and Aggarwal 1977)

(9) Wastewater = \$0.018/kL (\$0.062/1,000 gal), \$0.022/kg BOD (\$0.01/lb BOD), \$0.044/kg SS (\$0.02/lb SS). These costs are averages of values reported by Carroad (1975). The total wastewater cost is the sum of these costs for the snap bean wasteloads shown in Table 5, with the addition of cooling water for snap beans (Table 4) for the water and Hot-Gas blanchers

Table 7 shows the labor, capital-related, and utility and waste treatment costs for the four blanchers, and it shows the basis used for calculating these costs. Since the open mesh conveyor belts used in the Hydrostatic and Hot-Gas Blanchers probably require more maintenance than the conveying systems used in the Vibratory Spiral or water blancher, higher maintenance costs were used for the former. The costs of water and waste treatment for the Hydrostatic Steam Blancher were calculated from the wasteload of conventional steam blanching with flume cooling (Table 4). The water use and wasteload for flume cooling, using the quantity for snap beans shown in Table 4, were added to those of water blanching and Hot-Gas Blanching to get an overall cost of water and wastewater for these systems.

The low capital investment needed for a water blancher is the reason for its lowest cost of operation. The lower costs of steam, water and wastewater treatment for the Vibratory Spiral Blancher-Cooler as compared to the water blancher were insufficient to balance the lower costs associated with capital investment. A doubling of the combined cost of utilities and wastewater treatment would give the Vibratory Spiral Blancher-Cooler, a lower operating cost than that of the water blancher. The Hot-Gas Blancher's high cost is attributable mostly to high capital related costs, while that of the Hydrostatic Steam Blancher is because of capital related and steam costs.

No attempt was made in these calculations to account for the loss of vegetable weight when air cooling or Hot-Gas blanching is used. If frozen vegetables are valued at $\$440/10^3 \cdot$ kg ($0.20/lb), a 2% loss of yield would add the equivalent of $\$8.80/10^3 \cdot$ kg to the cost of blanching and cooling. Since frozen vegetables are marketed by weight, such a large penalty for air cooling cannot be economically justified. A change in the way frozen vegetables are marketed would be required to take full advantage of the wastewater reduction possible with air cooling. One should also note that at a price of $\$440/10^3 \cdot$ kg for frozen vegetables, the entire cost of blanching and cooling is about 1% of the cost of production. The small impact of blanching and cooling on the total cost of production gives the processor little economic incentive for capital investment in wasteload-reducing, energy-efficient blanchers.

Table 8 gives a comparison of the cost of the Vibratory Spiral Blancher (without cooler) and the water blancher (without flume) as they would be used for canning vegetables. All other conditions of the cost calculation remain the same. By removing the necessity of cooling, the fixed capital investment of the vibratory spiral equipment is reduced by 53%, while for the water blancher the removal of the flume reduces the fixed capital investment by 28%. The water blancher still

Table 8. Cost of blanching without cooling for Vibratory Spiral Blancher and water blancher

		Vibratory Spiral Blancher	Water Blancher
		Labor Costs ($\$/10^3 \cdot$ kg)	
(1)	Operating Labor	0.63	0.63
(2)	Supervisor, fringe benefits, etc.	0.41	0.41
		1.04	1.04
		Capital Related Costs ($\$/10^3 \cdot$ kg)	
(3)	Maintenance	0.33	0.08
(4)	Depreciation	0.65	0.16
(5)	Insurance, Taxes, etc.	0.52	0.13
		1.50	0.37
		Utilities and Waste Treatment Costs ($\$/10^3 \cdot$ kg)	
(6)	Steam	1.24	1.75
(7)	Electricity	0.01	0.01
(8)	Water		0.02
(9)	Wastewater	0.02[a]	0.02
		1.27	1.80
	Total Cost	3.81	3.21
		Fixed Capital Investment ($)	
	Purchase Cost	51,000	11,400
	Delivery	2,500	600
	Installation	10,200	2,300
	Floor Space	2,000[b]	1,700
	Indirect Costs	16,400	4,000
		$82,100	$19,600

[a] Wasteload was taken as that of a conventional steam blancher

[b] 7.5m^2

gives the lower cost of operation, and here again a doubling of the combined cost of fuel, water and wastewater cost would make the cost of operating the Vibratory Spiral Blancher about the same as that of the water blancher (A doubling in cost would be equivalent to approximately a 7% annual increase for ten years).

NOMENCLATURE

BOD	Biochemical Oxygen Demand, kg/10^3 of raw vegetable
C	heat capacity of vegetables or water, kJ/(kg · °C)
E_B	hydraulic wasteload of blancher, L/10^3 · kg of raw vegetables

E_C	hydraulic wasteload of cooler, $L/10^3 \cdot kg$ of raw vegetables
ΔH	heat of vaporization for water, kJ/kg
Q_H	heat added to blancher, kJ/kg of raw vegetable
Q_L	heat lost from blancher, kJ/kg of raw vegetable
SS	Suspended Solids, $kg/10^3 \cdot kg$ of raw vegetable
$(TS)_B$	Total Solids in blanched vegetables, % by weight
$(TS)_C$	Total Solids in cooled vegetable, % by weight
$(TS)_{EB}$	Total Solids in blancher effluent, % by weight
$(TS)_{EC}$	Total Solids in cooler effluent, % by weight
$(TS)_R$	Total Solids in raw vegetable, % by weight
t_1	temperature of raw vegetables, °C
t_2	temperature of blanched vegetables, °C
t_3	temperature of cooled vegetables, °C
tw_i	temperature of inlet cooling water, °C
tw_o	temperature of outlet cooling water, °C
W_v	feed rate of raw vegetables, $10^3 \cdot kg/hr$
W_{evap}	water evaporated from vegetable, $10^3 \cdot kg/hr$
Y_B	yield of blanched vegetables, % of raw vegetable weight
Y_C	yield of cooled vegetables, % of raw vegetable weight
ρ_B	density of blancher effluent, kg/L
ρ_C	density of cooler effluent, kg/L

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ENERGY INPUTS FOR PRODUCTION, PACKAGING AND TRANSPORTATION OF WINE

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ABSTRACT

Energy expenditure for wine during its processing, packaging, and transportation was studied; the study was based on data from a winery in upstate New York for the years 1974-75 *and* 1975-76. *It was found that the following quantities of energy are expended in each of the studied segments per case of twelve* 1/5 *gal. bottles: winery operation —* 6.10×10^4 *Btu; ingredients and processing aids —* 1.34×10^4 *Btu; packaging materials —* 1.76×10^5 *Btu; and transportation for distribution —* 2.78×10^4 *Btu. All four segments should be studied for their potential for energy conservation.*

INTRODUCTION

The oil embargo of 1973 has been the catalyst for numerous energy related studies. The ultimate aim of these studies is to conserve the nation's fossil energy supplies and reduce the dependence on foreign energy sources. Few studies on the energy consumption for wines can be found in the open literature. A study on the energy consumption in the U.S. food system (Anon. 1976a) revealed that three trillion Btu's were expended in 1971 for the manufacture of wines, brandy, and brandy spirits in the U.S.; electric energy was not included in this estimate.

The present study of energy usage for the production, packaging, and

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transportation of wine was undertaken primarily to obtain quantitative data and to determine the areas for energy conservation. The study was conducted in cooperation with a winery in upstate New York using data for the processing seasons 1974-75 and 1975-76. The winery produced table, dessert, and sparkling wines.

Energy Units

The energy expended is expressed in terms of British Thermal Units (Btu's). Virtually all the energy used in the U.S. is derived from fossil fuels; therefore, the energy figures in this study represent Btu's of fossil energy sources depleted.

Scope of the Study

Energy inputs for the production and packaging of wines were examined. To produce wines, a number of energy sources are utilized for the day to day operations in a winery; these include electricity and various fuels such as heating oil and propane. In addition, energy associated with various ingredients used for the manufacture of wine was also accounted for. These ingredients, such as N_2 for counter pressure in the transfer operations, and O_2 for flavor development in sherry, require energy for their manufacture; this energy is referred to as indirect energy input because it is usually expended not in the winery but elsewhere. Packaging materials such as bottles and boxes are also used in wineries; the energy expended for the manufacture of the packaging materials was also estimated. Energy for packaging may also be considered as an indirect input.

Energy data for cork and filter aid could not be located in the literature; for this reason, estimation of the energy expended for these items was not possible.

There are several stages in the distribution of wine and energy is expended at each stage. Data were available only for the transportation segment of wholesale distribution; the energy expended for this segment was estimated. It is emphasized that considerable energy is expended for retail sale of wine and at home prior to consumption; however, the task of estimating these magnitudes was not undertaken.

METHODS EMPLOYED

Direct Energy Usage in the Winery

Energy consumed in the winery was calculated from the inventories of the fuels: fuel oil number 2 and propane, and the electric meter readings. Calorific values of fuel oil number 2 and propane derived from the literature (Gatts *et al.* 1974) were employed to obtain the Btu's. Electrical energy, a secondary source, was converted to Btu's of fossil fuel taking into account the production efficiency of 29.4% (Summers 1971); in other words, 1 kwh = 11,600 Btu. The direct energy sources are required for the production of wine and operation of the facilities that are essential for the functioning of the winery. No attempt was made to determine the energy use for just the production of wines. In other words, the boundaries of the processing system were assumed to be those of the winery.

Energy for Packaging

Energy for the packaging materials: bottles, stoppers, aluminum foil, and cardboard cartons was estimated from literature data (Berry and Makino 1974; Hoddinott 1975). The required weight of each item was obtained with the help of winery personnel.

Energy for Ingredients and Processing Aids

Energy expended for the manufacture of N_2 and O_2 was estimated from data compiled by Myers (1974). Press aid was used for the extraction of grape juice. The energy for the press aid (paper) was assumed to equal that for the manufacture of cardboard and was estimated using the data of Berry and Makino (1974). Various alcoholic liquids, that were not made at the winery, were used for blending and fortifying wines. The energy for the manufacture of these alcoholic liquids was estimated from data in the 1972 Census of Manufactures (Anon. 1976b).

For sugar and SO_2, energy data were available in the form of Btu per one dollar value of the item in 1967 (Herendeen and Bullard 1974; Myers 1974); energy for SO_2 was assumed to equal that for sulfuric acid. To use these data, price of each item in 1967 was determined from various sources: sugar from Anon. (1970) and sulfuric acid from Anon. (1976c, 1977).

Reliable data were not available on the transportation modes and distances for the packaging materials and ingredients to the winery; data were available only for the alcoholic liquids. For this reason, the energy consumed for transportation was estimated only for the alcoholic liquids; transportation was by railroad and the energy intensity was taken as 721 Btu/ton-mile (Hirst 1973).

Energy for Transportation of Wine Cases

Trucks were the only mode of transportation for distribution of cases of wine; the energy intensity was taken as 2,540 Btu/ton-mile (Hirst 1973). Data on the cases of wine distributed to each of the mainland states were made available by the winery. Distances between the winery and each state were estimated from road maps assuming that the wine was delivered either to the most populous or centrally located city in a state; the choice depended on a state's population distribution.

RESULTS AND DISCUSSION

Energy is expended to grow grapes. Gunkel *et al.* (1974) estimated the energy expended in New York to grow grapes as equivalent to 27.4 gal. of gasoline per acre; they also estimated an average yield of 4 tons of grapes/acre. Based on these data and the quantity of grapes pressed, the energy for growing grapes was estimated as 8.15×10^{10} Btu; the calorific value of gasoline was taken as 1.25×10^5 Btu/gallon. From data on the distances between the vineyards and the winery, and assuming truck transportation energy intensity as 2,540 Btu/ton-mile (Hirst 1973), the energy for transporting the grapes to the winery was estimated to be 9.78×10^9 Btu.

Fuel oil number 2 employed for the generation of steam was the main fuel in the winery; in comparison, propane was consumed to a lesser extent and was used for operating fork lift trucks. Steam generated was used for processing needs and for heating buildings during cold weather. Electricity was used mainly for operating refrigeration and air-conditioning equipment, conveyor systems, and lighting. The total direct energy input for winery operations for the two years 1974-75 and 1975-76 was 5.68×10^{11} Btu; this translates to 6.10×10^4 Btu/case (of twelve 1/5 gal. bottles).

Consumption of fuel oil number 2 and electricity during each month in 1974 is shown in Fig. 1. As seen in the figure there is considerable variation, from month to month, for both energy sources. The consumption of fuel oil is high from November to April primarily due to heating requirements of the buildings; the high consumption in October is mainly due to increase in the use of steam during the processing of grapes. In contrast to the consumption of fuel oil, consumption of electricity is low during the winter months. The demand for air-conditioning increases the electricity consumption during the period May to September; the consumption is highest in October when grapes are processed.

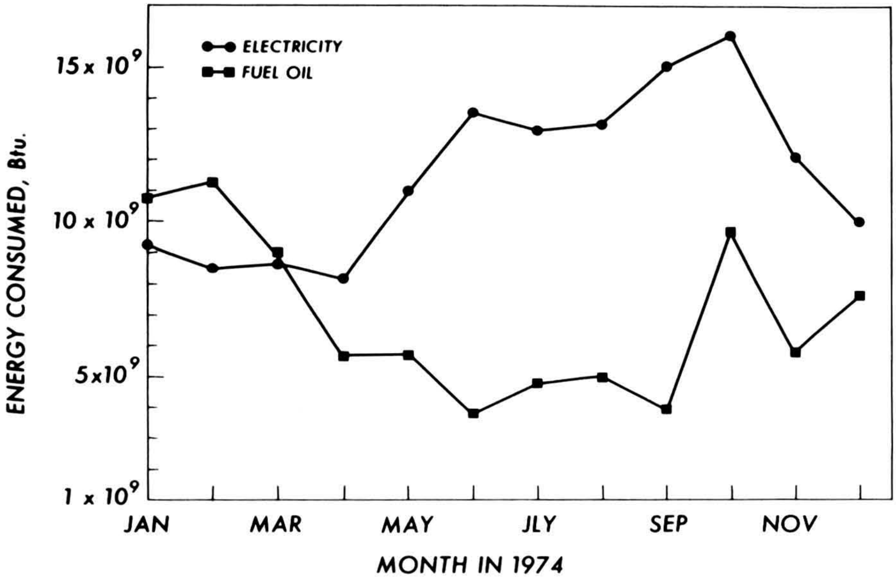

FIG. 1. ELECTRICITY AND FUEL OIL CONSUMPTION EACH MONTH IN 1974

For the same two years, energy (indirect) inputs via ingredients for the production of wine were as follows: sugar — 4.55 X 10^{10} Btu; N_2 — 8.55 X 10^8 Btu; O_2 — 1.51 X 10^8 Btu; press aid — 2.03 X 10^{10} Btu; alcoholic liquids — 5.81 X 10^{10}; and SO_2 — 6.80 X 10^7 Btu. The energy contribution due to all the ingredients and press aid is 1.25 X 10^{11} Btu or 22% of the magnitude of the direct energy consumed. An additional 4.81 X 10^{10} Btu were spent to transport the alcoholic liquids to the winery.

Previous studies have shown that packaging is very energy intensive (Berry and Makino 1974; Hoddinott 1975). The energy consumed for bottles was estimated to be 11.84 X 10^{11} Btu, which is more than twice the magnitude of the energy consumed directly in the winery. Assuming that each bottle is discarded after the consumption of wine, it can be seen that a large amount of energy is also discarded.

Energy expenditure due to cartons, stoppers, and other miscellaneous packaging materials totalled 4.53 X 10^{11} Btu. Of this total, cardboard boxes accounted for 3.11 X 10^{11} Btu while aluminum caps and capsules contributed 9.06 X 10^{10} Btu. The energy for all packaging materials: bottles, boxes, and caps, is nearly three times that expended directly at the winery. Conservation through recycling is being practiced by the paper and paperboard industries; therefore, there is reason to believe that some of the cardboard boxes are being recycled to some extent. There is little chance for the aluminum caps and plastic stoppers to be recycled, because of their small size which encourages their disposal as solid waste.

Energy expended during the transportation of wine to different states was also significant. For the two years, 1974-75 and 1975-76, the energy for transportation amounted to 2.59×10^{11} Btu. The use of railroads instead of trucks will lower the energy consumption to 7.35×10^{10} Btu, i.e., reduction by about 72%. These estimates are based on the energy intensiveness data of Hirst (1973).

Table 1. Energy inputs for wine: from growing grapes to distribution of wine for the yars 1974—75 and 1975—76

	Total Energy Input for Two Years Btu	Energy per Case,[1] Btu	As Fraction of Energy for Growing Grapes
Growing Grapes	8.15×10^{10}	8.75×10^{3}	1.00
Transport of grapes to winery	9.78×10^{9}	1.05×10^{3}	0.12
Winery operation	5.68×10^{11}	6.10×10^{4}	6.97
Ingredients and processing aids	1.25×10^{11}	1.34×10^{4}	1.53
Packaging materials	1.64×10^{12}	1.76×10^{5}	20.10
Transportation for wholesale	2.59×10^{11}	2.78×10^{4}	3.18

[1] Case of twelve 1/5 gal. bottles

The energy inputs from growing the grapes to the wholesale distribution of the wines are summarized in Table 1; the same data are also expressed as fraction of the energy expended to grow the grapes. It is obvious from Table 1 that among the various segments, the maximum energy input is due to packaging materials. However, they are not the only targets for conservation efforts.

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SIMULATION OF AN IMMOBILIZED ENZYME PARTICLE USING β-GALACTOSIDASE ADSORBED TO A PHENOL-FORMALDEHYDE RESIN

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ABSTRACT

The mass transfer and kinetic properties of both soluble and immobilized β-galactosidase were investigated. A reversible enzyme kinetic model was found to best fit the soluble and immobilized enzymatic lactose hydrolysis. A finite difference model was used to simulate the steady state and unsteady state behavior of an immobilized enzyme particle. The performance of the catalyst in a stirred tank reactor was simulated by using the physical properties of the support with the kinetic model and varying the effective substrate diffusivity to fit the data. A sensitivity analysis was performed to evaluate the effect of particle size, diffusivity, external mass transfer coefficient and enzyme loading.

INTRODUCTION

The application of heterogeneous catalysis principles to immobilized enzymes for food processes requires a careful evaluation of the entire reaction process. For catalysis in homogeneous solution, the mass transfer contribution to the overall reaction rate is often ignored. However, for supported catalysts, the mass transfer of reactants from the bulk phase to the catalytic site may be the rate-limiting step. An enzyme immobilized on a porous catalyst support can be treated as a heterogeneous catalyst. Immobilization of the enzyme can change the observed kinetics, either through the physical effects of mass transport or a change in the chemical responses of the enzyme. For design and

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optimization purposes, it would be useful to analyze the physical effects separately from the chemical effects. With this type of model, the effects of varying catalyst parameters (support size and shape, enzyme loading, substrate diffusivity) and reactor parameters (configuration, external mass transfer, mixing) can be evaluated in terms of the overall reaction rate. Process design would include determining the cost of each step of the process. Further research could then be concentrated on the areas of highest cost. This paper describes the use of a model for designing an immobilized enzyme reactor for a food process.

Diffusion and Reaction in a Catalyst Particle

There have been many efforts to separate external diffusion and internal diffusion effects from the chemical reaction rate for heterogeneous catalysts. Investigators often have given analytical solutions or have approximated the solution to the steady-state mass balance for diffusion and chemical reaction in a catalyst particle. For component C diffusing into a catalyst sphere and reacting, the unsteady-state mass balance for a concentration gradient in the radial direction only is:

$$\frac{\partial C_i}{\partial t} = D_i \left\{ \frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r} \frac{\partial C_i}{\partial r} \right\} - R(C_i) \qquad (1)$$

where C_i is the concentration of C in the fluid, t is time, D_i is the diffusivity of i in the particle, r denotes position, and $R(C_i)$ is the expression for the chemical reaction rate in the microenvironment corresponding to the position r. Equation 1 becomes the steady-state mass balance when the left-hand side equals zero. Equation 1 is analogous to Fickian diffusion plus chemical reaction and assumes constant diffusivity throughout the particle, a homogeneous medium for diffusion, and constant temperature. One of the common boundary conditions used to solve this equation involves assuming the concentration of reactant at the external surface of the catalyst to be constant. Analytical solutions to the steady-state equation are available for zero, first and second order rate expressions and for several geometries (Thiele 1939). Solutions are also available for some catalytic expressions of the Hougen-Watson (Langmuir-Hinschelwood) type, where equations are written for the adsorption, reaction and desorption steps and then are simplified based on the rate-limiting step (Knudsen *et al.* 1966; Roberts and Satterfield 1965; Roberts and Satterfield 1966).

The literature contains several reviews of immobilized enzymes (Stark 1971; Zaborwsky 1973; Gutcho 1974). Many different enzymes, such as glucose isomerase, amylase, urease and lactase, have been immobilized. The immobilization of lactase has sparked much interest due to the milk whey disposal problem. Lactase has been immobilized to many solid supports which include porous glass, stainless steel, phenol-formaldehyde resins, polyacrylamide gels and cellulose. The phenol-formaldehyde resin meets the criteria for a commercial system by being a stable, rigid and economical catalyst support. However very little work has been done to quantitatively evaluate its mass transfer and kinetic properties.

A few workers have adopted numerical techniques for solving the steady-state case and applied them to immobilized enzymes. Moo-Young and Kobayashi (1972) numerically integrated the steady-state mass balance equation to obtain solutions for four enzyme reaction schemes in a flat plate. They demonstrated that straight Lineweaver-Burk plots may result even though the effectiveness factor is much less than one. Kobayashi and Laidler (1973) and Kobayashi and Moo-Young (1973) developed a method for determining the true Michaelis-Menten parameters of an immobilized enzyme when internal diffusion has a large effect on the overall reaction rate. Wadiak and Carbonell (1975) have investigated the steady-state effect of coupled diffusion and reaction for substrate and product inhibition in a spherical particle with external mass transfer limitations.

Numerical Approximation by Finite Difference Methods

The above techniques have a number of limitations. They deal only with the steady-state case and do not treat the dynamic, unsteady-state case. The unsteady-state analysis would be helpful for determining the time required by the catalyst to reach steady-state operation in a given reactor especially when process variations take place. The concentration of reactant at the surface of the particle is usually considered constant. This assumption is valid only if the rate of external mass transfer is much greater than the overall reaction rate. The use of a flux boundary condition might be more appropriate. In some reactor configurations, mass transfer at the catalyst surface may be rate-limiting. Another more accurate boundary condition allows mass transfer by convection at the surface of the catalyst. With an appropriate mass transfer coefficient based on the geometry of the particle and conditions in the reactor, the mass transfer characteristics can be more accurately described.

The reaction rate in some previous solutions was dependent only on the reactant concentration. Many enzyme reaction rate expressions include terms affected by the product concentration, i.e., product inhibition and reversible kinetics. In these instances, the products often have diffusivities different from the diffusivity of the reactant and more than one partial differential equation must be considered.

In this simulation, a finite difference method was used to approximate the unsteady-state partial differential equations. The finite difference method allowed inclusion of an external mass transfer coefficient, rate equations with product and reactant terms, and different diffusivities for the product and the reactant. The kinetic rate expression could easily be changed without altering the basic program. Both the unsteady-state behavior of the catalyst and the steady-state response could be determined. The transient analysis shows not only the steady-state result but how it was achieved. It also allows evaluating the effects of time-dependent phenomena on catalyst performance (response to a step change in substrate feed concentration or temperature). This approach yields a very flexible model for process design.

MATERIALS AND METHODS

Materials

β-galactosidase (EC 3.2.1.23) was obtained from Wallerstein Company, Morton Grove, Illinois (Lactase LP Lot K6601) and used without further purification.

The porous phenol formaldehyde resin, Duolite ES-762, was donated by the Diamond Shamrock Company, Redwood City, California. The porous resin is reportedly stable to acids, bases, and most organic solvents; is granular, rigid, and resistant to attrition; has a pore volume of approximately .6cm^3 per cm^3 of resin, at least a pore size of 300 Å (Olsen and Stanley 1974), a surface area of approximately 100 m^2/cm^3, and a density of 1.11 to 1.3 g/cm^3. Duolite ES-762, commercially available as 50 mesh, was found to have a particle mesh size distribution of 5% (+80—70), 14% (+70—60), 51% (+60—48), 25% (+48—42) and 5% (+42—35).

Analytical grade reagents and deionized double-distilled water were used: β-D glucose, Calbiochem; Glucostat, Worthington Biochemical; lactose USP, Matheson Coleman and Bell; potassium sorbate, Sigma; all other chemicals, J.T. Baker.

Feed Preparation

Pure lactose solutions were prepared by weighing out the desired amount of lactose in double distilled water, adjusting the solution to pH 4 with lactic acid, and then adding distilled water to the desired volume.

Glucose Analysis

When analyzing for glucose all solutions were deproteinized when necessary with 1.8% $Ba(OH)_2 \cdot 8\ H_2O$ solution followed by 2.0% $ZnSO_4 \cdot 7\ H_2$), (Somogyi 1945) and then analyzed at 400 nm using Glucostat. The accuracy of the glucose analysis was found to be approximately 1/2% of the glucose present.

Soluble β-galactosidase Analysis

Data were obtained for conversion versus time at various enzyme concentrations at 40°C, pH 4.0. The pH of the lactose and enzyme solutions were adjusted with lactic acid and 0.1 N acetate buffer respectively. Five milliliters of the enzyme solution at 40°C were pipetted into 20 ml of 6.25% lactose solution at zero time (final solution 5% lactose). At timed intervals, 1-ml samples were removed and placed in a test tube contained in a boiling water bath for 3-5 min. The amount of glucose produced was used to determine the percent conversion. The data were then used to evaluate the constants for the enzyme reaction models.

A search subroutine using Rosenbrock's rotating coordinate search (Rosenbrock and Storey 1966) with several important modifications to speed convergence (Hershey 1970) was used to search for the best fit for Equation 2 to the conversion data. The reaction rate models were integrated and solved for $E \times t$, where E is the original enzyme preparation concentration, g/l and t is the time of reaction in seconds. The subroutine searched for the constants to minimize the sum of squares of the percent difference between the experimental value of $E \times t$ and the value calculated using the various searched constants in the integrated equations.

The optimized equation was used to calculate active enzyme concentration. Samples containing the unknown enzyme concentrations were diluted to approximately 0.1 mg enzyme preparation/ml. One milliliter of the enzyme solution (40°C) was pipetted into 4 ml of a 6.25% w/v lactose solution (40°C) at zero time. At 600, 1200 and 1800 sec 1-ml samples were removed and the reaction stopped by using Somogyi reagent (Somogy 1945). The samples were analyzed for glucose to determine the percent conversion. Knowing the conversion at a given time, the enzyme concentration was calculated using the integrated form of Equation 2. The enzyme concentration calculated for the various times was then averaged. The enzyme and lactose solutions were also analyzed for initial glucose content. The calculated enzyme concentrations are relative to the original known standards.

Immobilized Enzyme Reaction Studies

The enzymes were immobilized according to the procedure of Olsen and Stanley (1973). Five hundred ml of 5% lactose pH 4 solution was placed in a 1000-ml glass reactor and temperature was controlled to 0.1°C. The baffles in the reactor were one-tenth the reactor diameter and were made from 16 gauge stainless steel. Two stainless steel wire rings were silver-soldered to the baffles to keep them in place. A polyethylene impeller, approximately 1/3 the reactor diameter, was run at 200 rpm and controlled with a solid-state controller. Drained catalyst was preheated to 40°C and quickly added to the reactor. A catalyst volume of less than 0.1 the solution volume was used. When a 1-ml sample was to be taken, the stirrer was shut off for approximately 30 sec until the resin settled. The run proceeded until almost all the lactose was hydrolyzed which was approximately 24 hr.

Parameter Description

Numerical description of the physical parameters of the system was important. The critical physical parameters were particle shape and size, porosity and/or pore structure, enzyme loading, external mass transfer coefficients and internal mass transfer coefficients. For some rate expressions, the catalyst shape can have a large effect on the overall reaction rate (Aris 1957). The catalyst support was granular, but could be approximated by spheres. The average particle diameter was calculated by wet-screening the resin and determining the volumetric average particle size.

The parameters of porosity and internal diffusivity were lumped together. An ion exchange resin is often highly solvated during use and establishing the pore size distribution under these conditions would be difficult. The catalyst structure was assumed to be an open, porous matrix with no distinct pore walls.

The enzyme was assumed to be evenly distributed throughout the particle. Since the support was thought to be an open, homogeneous polymer matrix, it was assumed that no enzyme molecules were sterically blocked from the lactose. Enzyme loading was determined by measuring enzyme depletion from the coupling as discussed under soluble β -galactosidase analysis. Correlations for spherical particles were available for estimating an external mass transfer coefficient. A correlation which was applicable to small particles suspended in slurries was used (Calderbank and Moo-Young 1961).

Model Implementation

The finite difference method chosen for model implementation was the Saul 'yev method, modified as discussed by Carnahan (Saul 'yev 1964; Carnahan *et al.* 1969). The program was implemented in double precision arithmetic on an IBM 360 computer. To check the accuracy of the method, the total mass flux into the sphere as calculated by the program was compared to analytic solutions for unsteady-state diffusion (Carslaw and Jaeger 1947) and diffusion and first-order reaction (Crank 1965). For unsteady-state diffusion, the numerical approximation was less than 1% different from the analytic solution. The first-order reaction approximation was within 3% of the analytic solution. Detailed description of the model can be found elsewhere (Grulke 1975).

Two kinetic rate expressions, a reversible rate expression and a product inhibition rate expression, have been fit to galactosidase hydrolysis data. The reversible rate expression is as follows:

$$\frac{d\,C_p}{dt} = \frac{(k_1 k_3 C_S - k_2 k_4 C_p)C_E}{(k_2 + k_3) + k_1 C_S + k_4 C_p} \tag{2}$$

where C_p is the product concentration, C_S is the substrate concentration, C_E is the enzyme concentration, t is time and k_1, k_2, k_3, k_4 are the associated rate constants. When k_2 is zero, Equation 2 reduces to the product inhibition rate expression. When k_4 is zero, Equation 2 reduces to the simpler Michaelis-Menton model. Since both the product and substrate concentrations appear in the rate expressions, it was necessary to account for both substrate and product during unsteady-state simulation. Therefore, two unsteady-state mass balances were approximated simultaneously. They were of the form:

$$\frac{\partial C_i}{\partial t} = D_i \left\{ \frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r}\frac{\partial C_i}{\partial r} \right\} + R(C_i,C_j) \tag{3}$$

where C_i and C_j are the concentrations of different components, and the rest of the nomenclature is defined by Equation 1.

At the surface of the sphere, the flux to the surface by diffusion must equal the flux from the surface by convection. Therefore,

$$D_i \left.\frac{\partial C_i}{dr}\right|_{r=R} = k_{ext}\,(C_{i,bulk} - C_{i,surface}) \tag{4}$$

where R is the radius of the particle, $C_{i,bulk}$ is the concentration of the *i* component in the bulk solution, $C_{i,surface}$ is the concentration of the

i component in equilibrium with the exterior surface of the catalyst particle. It can be argued that the area for mass transport just inside the particle surface is different from the area just outside the surface because of the polymer matrix and attached enzyme. Equation 4 could include terms to correct for this difference if it is well-known. In this simulation, the effective diffusivity term was used to account for the change in effective area and the tortuosity of the catalyst. The right-hand side of Equation 4 was substituted for the approximation of the diffusive flux in the equations for the outermost node of the sphere. The partition coefficient of the solutes between the bulk fluid and the particle environment was taken to be one; i.e., no concentration "jump" was allowed at the interface.

The rate data had been obtained in a stirred tank reactor. The mass balance for this reactor is:

$$V \frac{d\,C_C}{dt} = -\,\text{rate}_{\text{catalyst}}\,V_{\text{catalyst}} \tag{5}$$

where V is the volume of the fluid in the reactor, V_{catalyst} is the volume of the catalyst, $\text{rate}_{\text{catalyst}}$ is expressed as moles per unit volume-time and $d\,C_C/dt$ is the change of concentration of component C in the reactor with time. The reaction rate of the catalyst is the rate of substrate reacting to product for the entire particle. To simulate the reaction using the computer program, the catalyst particle reaction rate was computed from the model for ten different conversion levels. Equation 5 was then integrated using the computed catalyst rates to find the time necessary to reach each level of conversion for the batch reactor. Nearly identical curves were obtained by computing the particle reaction rate for each time interaction in the program and then numerically integrating the mass balance (Equation 5) to update the concentrations of substrate and product in the vessel. For all the batch data, the catalyst volume to reactor volume ratio was kept less than 0.10 (the limiting ratio for maintaining quasi-steady-state operation of a heterogeneous batch reactor with first-order kinetics (Lewis and Paynter 1971)).

RESULTS AND DISCUSSION

Soluble β-galactosidase Kinetics

Five concentrations of Wallerstein β-galactosidase, from .040 mg

Table 1. % Conversion of lactose vs time (sec) at various enzyme concentrations

Initial Lactose Concentration — 50 mg/ml Temperature — 40°C
Enzyme Source — Wallerstein pH — 4.0

Time	% Conversion	Time	% Conversion	Time	% Conversion
Run 1	$E_o = 0.040$ mg/ml				
300	0.88	1500	3.24	3600	5.79
600	1.66	1800	3.73	5400	6.07
900	2.27	2100	4.22	7200	8.78
1200	—	2400	4.51	9000	9.93
Run 2	$E_o = 0.404$ mg/ml				
300	5.07	2400	18.74	4500	24.48
600	8.66	2700	19.72	4800	25.74
900	10.98	3000	20.91	5400	27.12
1200	13.09	3300	21.32	9000	34.14
1500	14.61	3600	22.15	12600	39.42
1800	15.97	3900	23.60	16200	45.24
2150	17.66	4200	23.85		
Run 3	$E_o = 2.04$ mg/ml				
900	26.87	9000	65.01	16200	75.86
1800	35.45	10800	68.15	18000	79.27
2700	40.89	12600	72.33	19800	82.80
5400	54.41	14400	75.08	21655	83.71
7200	59.26				
Run 4	$E_o = 9.945$ mg/ml				
300	40.30	1800	69.73	7300	90.89
600	50.30	2700	75.90	10800	94.92
900	55.30	3600	80.69	14400	95.55
1200	61.35	4500	82.70	18000	96.18
1500	64.11	5400	86.11	21600	96.81
Run 5	$E_o = 9.992$ mg/ml				
300	38.80	1800	69.60	7300	93.16
600	48.48	2700	76.18	10800	97.24
900	58.02	3600	82.76	14400	97.50
1200	61.76	4500	85.52	18000	97.24
1500	66.70	5400	87.10	21600	97.90

enzyme preparation/ml solution to 10 mg/ml, were used to hydrolyze a 5% lactose solution at 40°C, pH 4.0. Preliminary studies showed little or no enzyme deactivation under these conditions. The data for soluble hydrolysis given in Table 1 show that maximum conversion obtained was 97.5 ± .5% indicating that an equilibrium conversion may exist and that k_2 of Equation 2 may not be zero. Using the search technique described under the soluble enzyme analyses section, the constants found for the reversible and for the product inhibition models giving the best fit for the soluble data of Table 1 are given in Table 2 and compared with the constants calculated from the data of Woychik and Wondolowski (1972) using their proposed product inhibition model.

Table 2. Comparison of enzyme reaction model constants

Enzyme Model Constants	Irreversible Model	Reversible Model	Woychik and Wondolowski (1972)
k_1	-0.01948	0.4513×10^{-2}	0.6197×10^{-2}
k_2	0.0	0.7844×10^{-7}	0.0
k_3	0.1115×10^{-3}	0.1377×10^{-3}	0.1183×10^{-2}
k_4	-0.59498	0.1639	0.13123
K_S[b]	-0.5723×10^{-2}	0.3054×10^{-1}	0.180×10^{-1}
K_p[b]	-0.1874×10^{-3}	0.8406×10^{-3}	0.849×10^{-3}[a]
V_1[c]	0.1115×10^{-3}	0.1377×10^{-3}	0.1183×10^{-2}
V_2[c]	0.0	0.7844×10^{-7}	0.0

[a] calculated from reported data
[b] moles/liter
[c] moles of glucose produced/(min) (g of enzyme preparation)

A comparison of the constants for the two models show that two of the constants found for the irreversible model are negative which is a meaningless result while the constants found for the reversible model closely match those calculated from Woychik and Wondolowski (1972). Based on the data, the activity of the enzyme used in this work was 10% of the activity of Woychik and Wondolowski's enzyme. Since the literature data were obtained with pure enzyme, their value for k indicated that the preparation used in this work is approximately 10% enzyme.

Woychik and Wondolowski (1972) obtained their data from initial rate studies with variations in galactose concentration approximating only up to 50% conversion. However, at high conversions the reversible term may become important. In Fig. 1, a significant deviation from the actual data occurs when using the constants of Woychik and Wondolowski (1972) at high conversions as compared to the reversible model constants. Therefore, it is important to consider the total range of conversions and conditions when attempting to model an enzyme reaction.

Although the reversible model is apparently a good fit for the data investigated, it is not an all encompassing model. The search technique gave four constants that fit the data. Possibly four totally different

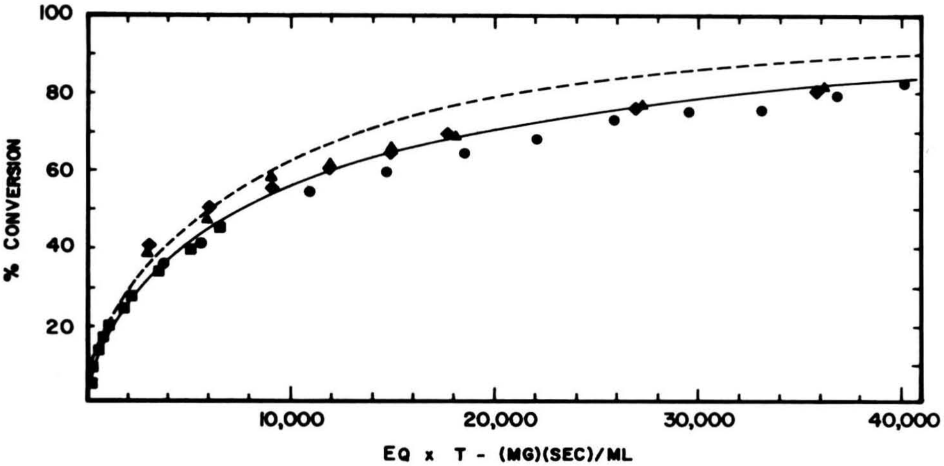


FIG. 1. SOLUBLE ENZYMATIC HYDROLYSIS OF A 5% LACTOSE SOLUTION

———————— Reversible Equation
-------------------- Woychik and Wondolowski Equation
E_o = 9.945 mg/ml
E_o = 9.99 mg/ml
E_o = 2.04 mg/ml
E_o = 0.404 mg/ml

values could be found to also adequately fit the data. Therefore, any conclusions about individual constants cannot be justified without further study. The concentration of water needed for hydrolysis was lumped into the constants since it is relatively high and will not change significantly. The concentration of glucose was neglected in the model since it does not inhibit the reaction. Side reactions may involve two galactose molecules or other molecules to form a variety of oligosaccharides which will affect the true kinetics (Okos 1975).

Immobilized Reactor Studies. Immobilized β-galactosidase catalysts were made with −16/+18 mesh particles and −50/+60 mesh particles. Batch hydrolysis of 5% lactose solutions was done at 40°C and pH 4 in a stirred tank reactor as previously described. The catalyst was added to 0.5 liters of lactose solution. The percent conversion of the lactose solution was measured in terms of glucose production as shown in Fig. 1. The physical parameters of the catalysts are listed in Table 3. The volume of the catalyst was taken to be the volume of the particles themselves as computed from their density and weight.

Computer Simulation Studies. One purpose for modeling the immobilized enzyme data was to determine the effects of internal

Table 3.

Property	Catalyst I	Catalyst II	Catalyst III
g enzyme/liter catalyst	38.9	46.8	133.
Mesh size	−16/+18	−50/+60	−50/+60
Volume of catalyst, liter	0.0152	0.0151	0.0153

diffusion on overall reaction rate. Since the product of the reaction, galactose, affected the rate, the build-up of galactose in the particle would affect both the steady-state and the unsteady-state reaction rates of the catalyst. The amount of galactose which would build up in the particle depended on the particle size, the diffusivity and the reaction rate. Figure 2 shows the unsteady-state build-up of galactose in a 35 mesh particle when the enzyme concentration equals 133 g enzyme/l catalyst, the soluble enzyme reversible kinetics are assumed and the catalyst surface is operating under zero conversion conditions (substrate concentration at the particle surface is kept at 5% lactose by weight and product concentration is kept at zero). The diffusivities used were the diffusivities of lactose and galactose in free solution. These are the highest diffusivities to be expected since steric hindrance to diffusion within the catalyst particle will decrease the diffusivities. The product concentration builds up first near the surface of the particle since the product is being generated while the substrate is diffusing into the particle. As substrate diffuses to the interior of the particle and reacts to generate product, the galactose level rises at the center of the particle. At steady-state, the product levels are highest in the center of the particle and decrease toward the surface.

The effectiveness factor for the catalyst can be defined as the actual reaction rate divided by the reaction rate expected if all catalytic sites were exposed to the external environment of the particle. Figure 3 shows the effectivenss factor plot of the above catalyst exposed to 5% lactose solution at 40°C. The effectivenss factor is much less than one for low conversions, but increases as the conversion approaches equilibrium. This increase is due to the large reduction in the chemical reaction rate when product is present. Even though more product is present within the support at high conversions, the over-all rate is less affected on a percentage basis because the chemical reaction rate is becoming slower relative to the mass transfer rate. Based on Fig. 2 and 3, it appeared likely that the enzyme reaction could be diffusion-limited, particularly at low conversions. At low conversions, the catalyst effect-

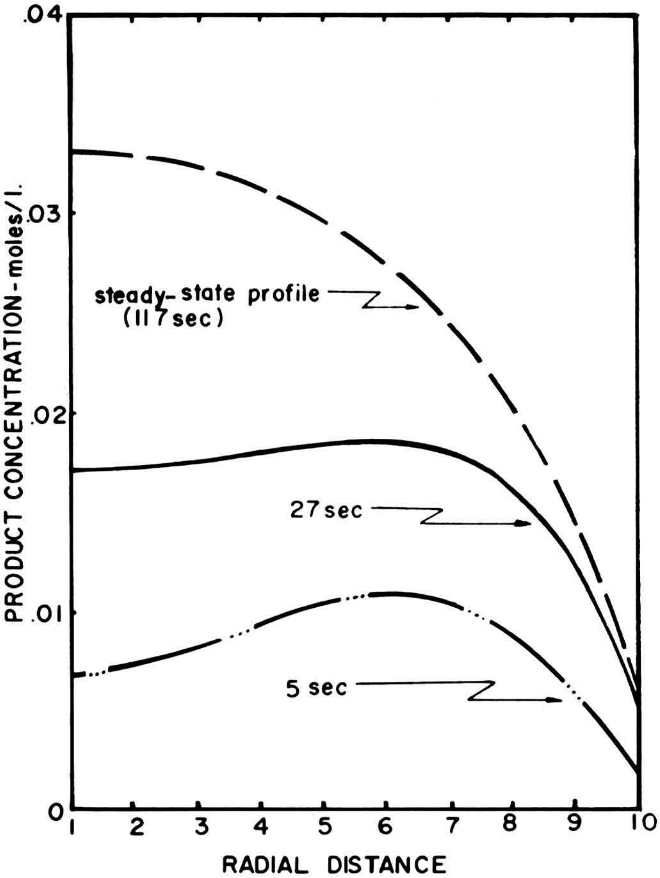


FIG. 2. UNSTEADY-STATE BUILDUP OF GALACTOSE WITHIN A 35 MESH CATALYST PARTICLE

C_{E_0} = 133 g enzyme/liter catalyst, C_{S_0} = 5% lactose, C_{P_0} = O, D_{Lactose} = 4.9 X 10^{-6} cm^2/sec. R=1 is the center node of the particle and R = 10 is the outer surface node.

iveness factor is low. Enzyme assays performed only at low conversions would yield misleading information about the number of active sites. Figure 3 illustrates the importance of obtaining data over a range of conversions with this catalyst.

Determining Effective Diffusivity

Previous workers indicated that a product inhibition rate expression can be used to describe lactose hydrolysis by β-galactosidase immobilized on porous glass (Woychik and Wondolowski 1972). For the soluble enzyme data, rate constants for the product inhibition and reversible rate expressions were found by using a computer search technique described earlier as given in Table 2. Both the searched product inhibition expression and the reversible rate expression fit the soluble data at all conversions. It is interesting to note that some of the rate constants of the product inhibition model have to be negative to fit the data.

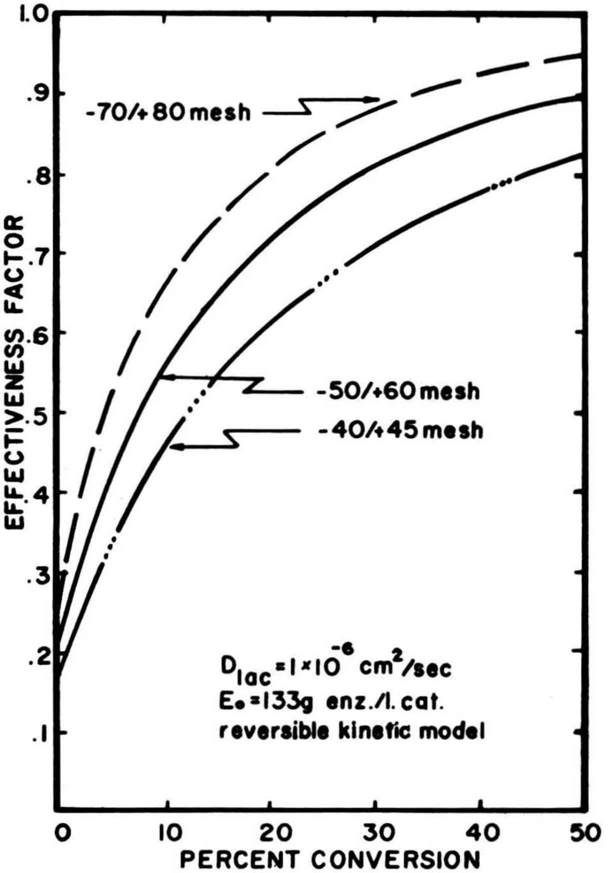


FIG. 3. EFFECTIVENESS FACTOR AS A FUNCTION OF CATALYST PARTICLE SIZE

C_{Eo} = 133 g enzyme/liter catalyst.

For purposes of modeling, $R(C_i,C_j)$ in Equation 3 was replaced by the proper kinetic function with its associated constants. The external mass transfer coefficient was computed from the correlation by using the properties of a 5% lactose solution. The ratio of lactose diffusivity to galactose diffusivity was kept constant ($1/\sqrt{2}$) as both compounds are relatively small in size and as lactose is twice the molecular weight of galactose (Geankoplis 1972).

Production inhibition (irreversible) kinetics of Table 2 were used first to fit the data of the immobilized β -galactosidase. The immobilized enzyme data was modeled by assuming that the soluble enzyme kinetics described the insoluble enzyme kinetics, using the physically measured enzyme loading and particle diameter, computing the external mass transfer coefficient, and varying the internal diffusion coefficients to fit the data. For the measured particle size, there was no diffusivity lower than 4.9×10^{-6} cm^2/sec which could fit the data. For diffusivities in this range, the predicted conversion-time curve always fell below the data, i.e. the real catalyst reached a given conversion faster than the model. A diffusivity smaller than the soluble substrate diffusivity would seem reasonable since there might be steric hindrance to diffusion within the support. On the basis that the assumed particle size was greater than the effective particle size, the particle size was decreased (with $D_{\text{Lactose}} = 4.9 \times 10^{-6}$ cm^2/sec) until the integrated conversion versus time curve fell above the data. This first occurred when the particle diameter was one-half the value determined by wet screening. Figure 4 shows the soluble data, the insoluble data and the predicted insoluble enzyme reaction curve under these conditions. Above 60% conversion, the model converges toward the soluble enzyme data. Since neither varying the diffusivities or particle size gave reasonable fits, it was decided that the product inhibition kinetic model did not adequately describe the kinetics.

The reversible rate expression was then used to fit the insoluble enzyme rate data. The particle size was assumed to be the wet-screen diameter, the other parameters were kept as before and the diffusivities of the substrate and product were varied to fit the data. After varying the diffusivity, the best fit was found to be for an effective diffusivity of lactose of 1.0×10^{-6} cm^2/sec, a factor of 5 lower than the free solution diffusivity. Figure 5 shows the data and the computed conversion versus time curve. Using this same diffusivity, conversion versus time curves were predicted for data taken with different catalysts. The predictions are based on the measured enzyme loading and particle size for each catalyst, with all other parameters being the same. The data and model predictions are given in Fig. 6. The diffusion model predicts slightly longer times for low conversion values than are actually observed. For an enzyme loading of 39g enzyme/l catalyst and 40% conversion, the model prediction is 15% higher than the observed batch time.

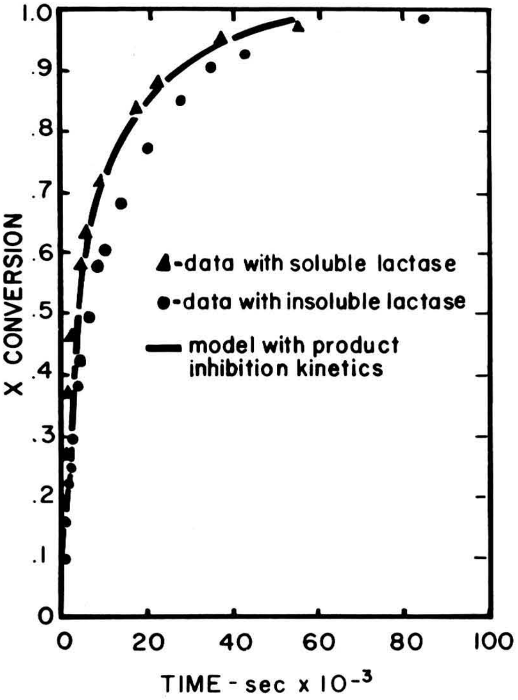
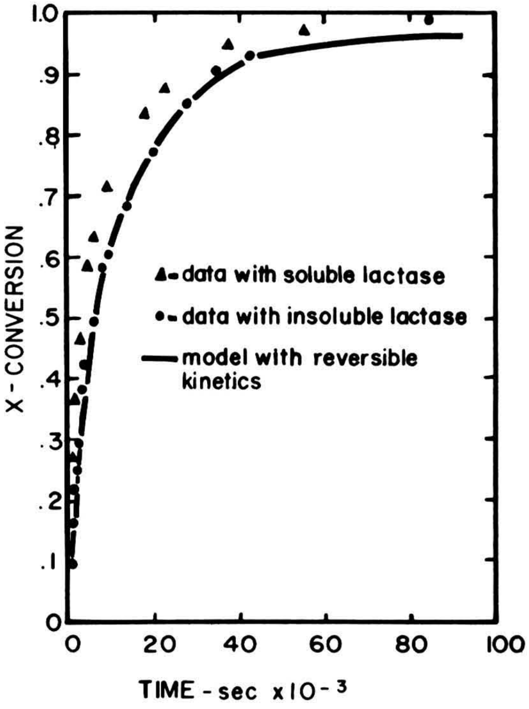


FIG. 4. DIFFUSION AND REACTION MODEL USING THE PRODUCT IN—HIBITION KINETIC MODEL (CATALYST I)

FIG. 5. DIFFUSION AND REACTION MODEL USING REVERSIBLE KINETIC MODEL (CATALYST I)



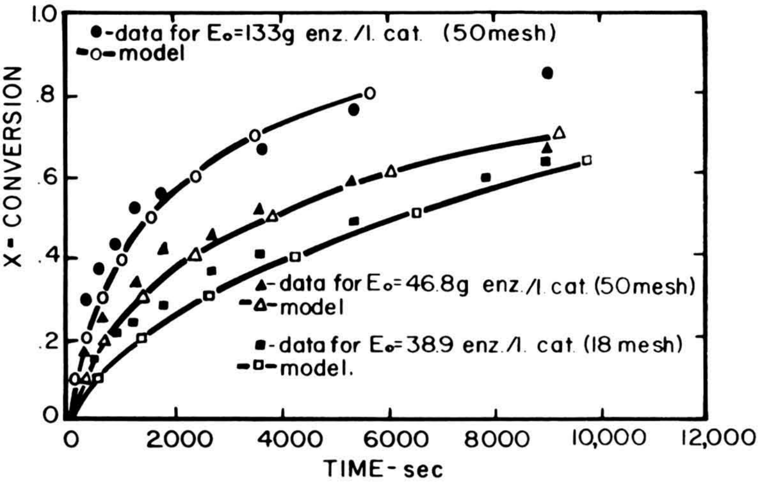


FIG. 6. DIFFUSION AND REACTION MODEL PREDICTIONS FOR DIFFERENT CATALYSTS

It may be argued that the use of soluble enzyme kinetic rate expressions for immobilized enzymes is incorrect unless the kinetics of the immobilized enzyme have been isolated and are known to be the same as the soluble enzyme kinetics. Changes in enzyme kinetics have been observed upon immobilization by many investigators. Degradation may also occur during and after the immobilization process. The catalysts simulated in this study had high enzyme loadings relative to previous work. It is possible that enzyme-enzyme interactions were more important than enzyme-support interactions, thereby, reducing degradation and changes in the observed kinetics. Previous work indicated that very little enzyme was deactivated upon immobilization. A comparison of soluble data and the data of catalyst II (46.8 g enz/liter cat) on a E X t versus conversions plot showed very little differences (Okos 1975). Based on the predictive capability of the model, the soluble enzyme kinetics represent at least a good approximation to the insoluble enzyme kinetics.

Parameter Sensitivity of the Model

The basic model was perturbed to demonstrate the effects of particle size, diffusivity, external mass transfer coefficient and enzyme loading parameters on reactor design. External diffusion to the particle from the bulk solution did not seem to be rate-limiting under the reaction conditions of these experiments. Varying the external mass transfer coefficient within the range predicted by the correlation had little effect on the integrated reactor curve for the batch reactor.

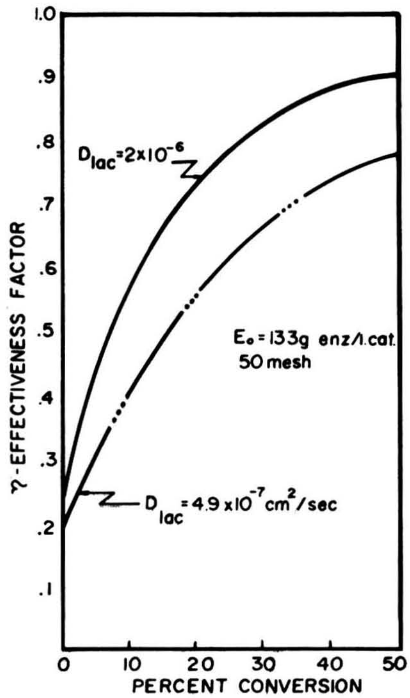


FIG. 7. THE EFFECT OF DIFFUSIVITY ON THE EFFECTIVENESS FACTOR

Varying the internal diffusion coefficient did affect reactor size. Figure 7 shows the effect of diffusivity on the effectiveness factor for an enzyme loading of 133 g enzyme/liter catalyst and a particle size of 50 mesh. At low conversions, both diffusivities yield low effectivensss factors. As conversion increases, the average product concentration in the particle increases, resulting in slower reaction rates. With higher values for the diffusivity, there is a lower product concentration gradient and therefore, less reduction in reaction rate.

The effect of internal diffusivity on reactor size is shown in Fig. 8 using a high enzyme loading and a 50 mesh particle. Because the reaction is reversible, higher conversions require very large reactors. The curve with $D = \infty$ represents the soluble enzyme case. At 60% conversion, a change in substrate diffusivity from 1×10^{-6} cm^2/sec to 5×10^{-7} cm^2/sec requires a 14% larger reactor. For larger particles, the effects of changing substrate diffusivity would be more pronounced. A change in the substrate diffusivity within the support can be achieved by changing the tortuosity and porosity of the support, or enzyme loading.

The effect of changing particle size on reactor size is shown in Fig. 9. At 60% conversion, a 30 mesh catalyst would require 17% more catalyst volume than an 80 mesh catalyst (this does not include the influence of packing factors on the void space between the particles). The effect of catalyst particle size distribution on the computed reactor size was evaluated. The catalyst which was listed as −50/+60 mesh actually contained a range of particle sizes from 80 mesh to 35 mesh. The average particle size of 50 mesh was calculated by averaging the volume fractions, determining an average particle volume and finding the radial size of the average particle volume. This radius was very close to a 50 mesh particle radius. After modeling was complete, the reaction rate of each volume fraction was computed and the total reactivity of the catalyst was determined. The reaction rate of the catalyst based on the average particle volume was within 2% of the reaction rate as computed by the volume fraction method over the entire conversion range. For these parameters and this catalyst, it seems that the average particle size based on a volume average can be used to predict catalyst activity.

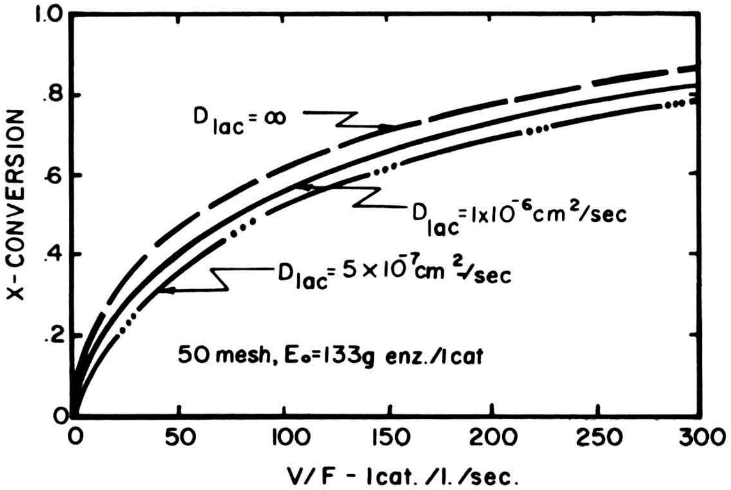


FIG. 8. THE EFFECT OF DIFFUSIVITY ON REACTOR SIZE

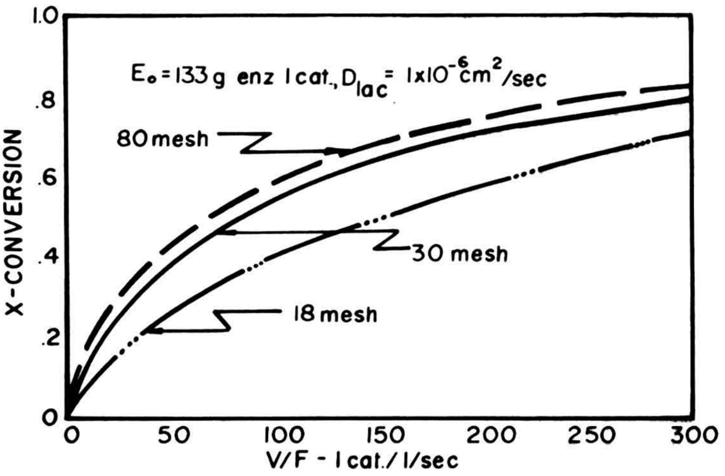


FIG. 9. THE EFFECT OF PARTICLE SIZE ON REACTOR SIZE

Enzyme loading has a large effect on reactor design. Figure 10 shows the effect of a 20-fold change in enzyme loading on reactor size. Choice of the most economical reactor design depends on the prices of the

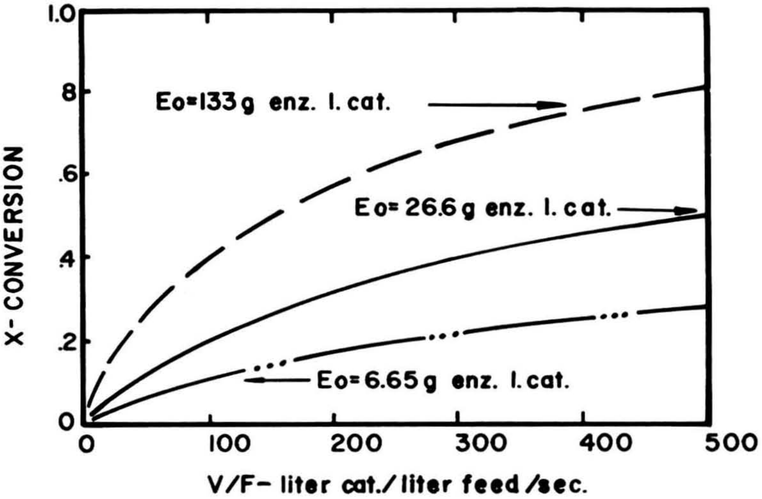


FIG. 10. THE EFFECT OF ENZYME LOADING ON REACTOR SIZE

enzyme and the support. For modeling purposes, the enzyme was assumed to be uniformly distributed throughout the particle. Since the enzyme was attached via a diffusion-sorption process, the enzyme may not be uniformly distributed. For comparison purposes, reaction rates were generated for a catalyst having an enzyme loading which increased from zero linearly with radial distance and which had an average of 133 g enzyme/liter catalyst. Enzyme loading was assumed to be highest at the surface. Figure 11 shows a comparison of reactor size for the surface-loaded catalyst and the uniformly loaded catalyst. Since more of

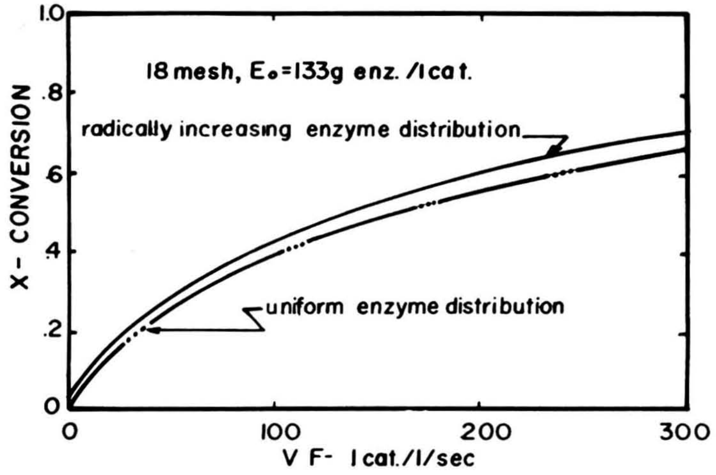


FIG. 11. THE EFFECT OF ENZYME DISTRIBUTION WITHIN THE CATALYST PARTICLE ON REACTOR SIZE

the enzyme is near the surface, the surface-loaded catalyst is less affected by diffusion and has a faster rate. At high conversion, diffusion becomes much less important and the differences between the reaction rates is very small.

The effective diffusivity of lactose in the catalyst support was determined at the highest enzyme loading and therefore, should include the highest tortuosity. For lower enzyme loadings, the tortuosity may be less and the diffusivities should be higher. If higher diffusivities had been used for the lower enzyme loadings, the predicted curves would shift toward the data at low conversion, resulting in a better fit. If the catalyst was surface-loaded and the enzyme distribution was included in the model, the predicted curves would also shift closer to the data.

CONCLUSIONS

The finite difference model was useful for approximating two simultaneous partial differential equations. The measured physical properties of the catalyst could be used along with a kinetic model of the enzyme and one variable, the effective diffusivity of the substrate, to simulate the performance of the catalyst in a stirred tank reactor. Integral reactor size was most sensitive to enzyme loading, substrate diffusivity and particle size. External mass transfer seemed to have little effect on the overall reaction rate. This type of model will find applications in modeling enzyme catalyst systems in which two different chemical species having different diffusivities affect the enzyme kinetic rate.

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LITERATURE ABSTRACTS

ABSTRACTS FROM ASHRAE TRANSACTIONS

Each of the following abstracts has been reprinted with permission from *Journal of Texture Studies.*

BRUISING AND ENERGY DISSIPATION IN APPLES. J. E. Holt and D. Schoorl. *J. Texture Studies* 7 (4), 421—432 (1976).

A strong correlation was obtained between bruise volume and energy absorbed for both impact and slow compression of Granny Smith Apples. Apple tissue was more easily bruised by slow compression than by impact. For the same amount of energy, bruise volumes were approximately 40% higher under slow compression.

There was no correlation between the stiffness (force/deflection) of apple flesh and bruise volume. It is unlikely that the theories of failure based on the theory of elasticity will prove useful in predicting the extent of bruising. The application of elastic theory to bruise initiation was not studied in this paper.

A simple model was formulated to explain the behavior of apples under compression. Apple tissue was likened to an orderly arrangement of liquid-filled, spherical cells bounded by viscoelastic membranes with air-filled interstitials. It is postulated that on initial compression the cells are deformed into ellipsoids under a stress distribution similar to that found in an elastic sphere. Further compression would then result in cell wall fracture, i.e., cell bursting in regions of high shearing stress. Distortion and bursting of cells explains the energy dissipative mechanism.

The work showed that energy absorbed during compression is a good predictor of bruising and is, thus, a useful parameter in evaluating handling and packing systems.

CONSIDERATIONS OF A GENERAL RHEOLOGICAL MODEL FOR THE MECHANICAL BEHAVIOR OF VISCOELASTIC SOLID FOOD MATERIALS. M. Peleg, *J. Texture Studies* 7 (2), 243—255 (1976).

A model describing the rheological behavior patterns of solid foods is suggested and discussed. It consists of a parallel array of a generalized Maxwell body in which the Maxwell elements have been modified by incorporation of two fracture elements. The model enables the anticipation of response patterns of real food materials under various force-deformation histories without becoming inconsistent. It also predicts the viscoelastic phenomena of materials after their failure and does not exclude the elastic deformation stage. The effects of experimental conditions, differences between various types of foods, as well as variations and changes in the same food can be expressed or explained in terms of model components and their relative distribution. The application of the model is demonstrated with a small number of representative elements.

RHEOLOGICAL PROPERTIES OF PECTATE GELS. J. R. Mitchell and J. M. V. Blanshard, *J. Texture Studies* 7 (3), 341—351 (1976).

Creep compliance measurements were made on calcium pectate gels using a parallel plate viscoelastometer. Linear viscoelastic behavior was observed and the response was consistent with a model containing a Maxwell element in series with three Voigt elements. When gels were prepared with the calcium level necessary for maximum gel strength a linear relationship was found between the reciprocal of the creep compliance and the square of the polysaccharide concentration.

The rheological behaviour of pectate gels had many similarities to gels prepared from alginates containing a high proportion of guluronic acid residues. However, pectate gels were more sensitive to calcium ions that alginate gels and at high calcium levels the Newtonian viscosity of the pectate gel was much higher than that found for the alginates. These differences have been interpreted in terms of the structure and molecular weight of the two polymers.

REVIEW PAPER — RHEOLOGY OF GELS. J. R. Mitchell, *J. Texture Studies* 7 (3) 313—339 (1976).

This review covers the rheology of gels formed by macromolecular food additives. In particular agar, alginate, carrageenan, gelatin, pectin and microbial polysaccharide gels are considered. Empirical and fundamental techniques that have been applied to gels are listed and the relationship between rheological parameters and sensory assessment of texture is briefly discussed. Certain general conclusions about the dependence of the rheological properties on network composition and structure are put forward.

THICKENING OF SOY PROTEIN SUSPENSIONS WITH CALCIUM. Cheryl Ho-Lee and Chokyun Rha, *J. Texture Studies* 7 (4), 441—449 (1976).

The objective of this study was to increase the apparent viscosity of 1—7% soy protein suspensions using calcium. The thickening effect, measured by apparent viscosity, depended upon the calcium concentration. Maximum apparent viscosity was obtained with a calcium to protein molar ratio of 20—50 moles of calcium required per mole of protein (M.W. 100,000) decreased with an increase in the protein concentration. Effective stirring was necessary during and after calcium addition to attain maximum thickening and stability. Heat treatment of the protein suspension prior to calcium addition enhanced the extent of apparent viscosity increase. Higher protein concentration, improved stability of the thickened mixture. The established optimum thickening conditions leading to a stable homogeneous suspension involved addition of 12.5mM $CaCl_2$ to 5% protein suspension preheated at 80°C for 30 min.

RHEOLOGICAL PROPERTIES OF ALGINATE GELS. J. R. Mitchell and J. M. V. Blanshard, *J. Texture Studies* 7 (2), 219—234 (1976).

Rheological properties of alginate gels formed in various ways were studied using a parallel plate viscoelastometer and an Instron.

All the gels studied exhibited linear viscoelastic behaviour. The creep compliance-time response was fitted by a model consisting of a Maxwell element in series with two or three Kelvin—voigt elements. Despite the fact that alginate gels are non-thermoreversible the crosslinks do not appear to be permanent. Gels formed with an alginate containing a high proportion of mannuronic acid residues are weaker and more elastic than gels prepared with an alginate predominantly composed of guluronic acid residues. When the level of calcium in the gel was high, the reciprocal of the creep compliance was proportional to the square of the polysaccharide concentration. A reduction in calcium level for a given polysaccharide concentration resulted in a more elastic gel. The nature of the temperature dependence varied with the degree of crosslinking and time of measurement after application of stress. The results were explained by assuming that the creep compliance could be regarded as the sum of two components: a time independent factor given by the theory of rubber elasticity, or some modification of this, and a time dependent factor associated with the breakage of crosslinks

COMPRESSION AND RELAXATION PROPERTIES OF CARROTS. L. J. Segerlind, B. A. Snobar and D. R. Heldman, *J. Texture Studies* 7 (4), 451—456 (1976).

Compression force and relaxation properties of radially compressed carrot samples were determined as a function of the cortex moisture content. The compression force at 10% deformation increased with an increase in the moisture content. The compression force at 76% moisture was almost ten times greater than the value at the 76% level. Similar trends were observed for part of the viscoelastic coefficients.

ABSTRACTS FROM THE AICHE JOURNAL

Each of the following abstracts has been reprinted with permission from the *AICHE Journal.*

MEAN TEMPERATURE DIFFERENCE: A REAPPRAISAL. K. Gardner and J. Taborek, AICHE *J* *23* (6), 777—785.

The derivation of the mean temperature difference in heat exchangers is based on a number of assumptions or idealizations, the most important ones being that the heat transfer coefficient is constant throughout the exchanger; that the temperature of either fluid is constant over any cross section of its nominal path, that is, complete mixing, no stratification or bypassing; and that an additional assumption for shell and tube exchangers, which has not always been fully recognized, is that within one baffle crossing the shell fluid temperature change is small with respect to its overall change, (that is, number of baffles is large). In actual exchangers, any of the above assumptions are frequently subject to various degrees of invalidation. This paper examines the effects of deviating from the first two assumptions and presents a new solution to the third.

AERATION AND MIXING IN DEEP TANK FERMENTATION SYSTEMS. J. L. Jackson and C. C. Shen, AICHE *J.* *24* (1), 63—71 (1978).

Oxygen transfer characteristics for three sizes of equipment, from 76 mm to 7.6 m in diameter and for liquid depths from 4 to 21 m, correlate well and permit sealing of fermentation systems in size. Simple orifice inlets for gas flow, uniformly distributed over a tank bottom, effect rapid mixing and permit very high oxygen demands to be met. Supersaturation provides dissolved gases for the flotation and solids separation as an inherent processing procedure. Nearly uniform bulk liquid composition and a linear decrease of gas phase composition with depth permit a proper, integrated value of the oxygen saturation driving force to be employed. Results provide the design basis for large scale aeration systems which offer potential savings in both capital and energy.

SYNTHESIS OF KINETIC STRUCTURE OF REACTION MIXTURES OF IRREVERSIBLE FIRST-ORDER REACTION. H. H. Lee, AICHE *J. 24* (1), 116—123 (1978).

A synthesis method for the kinetically consistent structure of reaction mixtures is developed based on elementary structures of reaction mixtures and rate expressions for product lumps of n^{th} order. Knowledge of product lumps and experimental kinetic data on each of the lumps are required for the synthesis of kinetic structure. Rate constants for all reaction paths and initial lumps from which all the product lumps originate can be determined.

REAL-TIME ESTIMATION OF AEROBIC BATCH FERMENTATION BIOMASS CONCENTRATION BY COMPONENT BALANCING. D. W. Zabriskie, and A. E. Humphrey, AICHE *J. 24* (1), 138—146 (1978).

Real-time estimates of biomass concentration and growth rate in fermentation processes were obtained by performing a material balance on oxygen and employing a kinetic model for molecular oxygen utilization. A model containing yield and maintenance terms were satisfactory in fermentations where only the EMP and TCA pathways were utilized for glucose metabolism. However, model alterations based on metabolic energetics were required before accurate estimates were obtained for a metabolically complex fermentation producing bakers yeast.

ABSTRACTS FROM ASHRAE TRANSACTIONS

Each of the following abstracts has been reprinted with permission from the American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc.

PRODUCT LOAD CALCULATION IN FOOD STORAGE. W. T. Pentzer, A. H. Bennett and G. G. Dull., *ASHRAE Trans. 83* (1), 519—524

This paper provides information on the thermal properties of food that are used to calculate refrigeration loads. Factors affecting product load such as precooling or freezing as part of the storage operation are discussed. The variability in the composition of foods, particularly in water content and its effect on thermal properties is emphasized. The reader is cautioned that tables of thermal properties are applicable only to foods of the specified water content. Beef, for example, may have a water content of the leanest grade with 27% fat. Avocados of the first picking may have 82% moisture content whereas the last picking made 6 months later has a moisture content of 65%. Heat of respiration of fruits and vegetables is shown to be extremely variable. Respiration rates differ between commodities, cultivars, location where grown, harvest maturity, time since harvest and length of storage period. Temperature has an over-riding influence on respiration rates, causing them to increase one to eight-fold for energy 10°C rise in temperature within certain limits from about 0°C to 27 to 30°C.

RELATIONSHIPS BETWEEN WATER CONTENT, ENTHALPY, SPECIFIC HEATING AND THERMAL DIFFUSIVITY OF FOODS. R. W. Dickerson, Jr., *ASHRAE Trans.* *83* (1), 525—532.

Water content has a pronounced effect on thermal properties of foods because foods consist chiefly of water. It is the water that must be frozen or thawed, and, primarily, it is the water, or ice, that has the major influence regarding heat transfer through the food. The chemical condition of the water also affects the heat transfer characteristics of the food. If the water contains significant amounts of material in solution, the freezing point is lower than that of water, and the removal of latent heat occurs over a wide range of temperature. Conversely, if the water in the food does not contain significant amounts of material in solution, the freezing point is very close to that of water, and the removal of latent heat occurs over a narrow range of temperature. For fresh foods, both specific heat and thermal diffusivity are a function of water content, and the values range from 40% to 90% of similar values for water depending on the water content of the foods.

THERMAL CONDUCTIVITY DATA FOR FOODS. C. P. Lentz and B. L. VandenBerg, *ASHRAE Trans.* *83* (1), 533—540 (1977).

The characteristics of the thermal conductivity of foods, methods of estimating thermal conductivity where complete data are not available, and potential sources of errors in estimating rates of heat transfer in foods are discussed with a view to assisting in the best use of available data. The large amount of conflicting data and the continuing shortage of needed reliable data can be explained on the basis of the wide variability and heterogeneity of many food substances, as well as the continuous development of new foods, refrigeration processes, and forms of packaging. Several methods of estimating the thermal conductivity of mixtures are discussed. The close relation between thermal conductivity and water content and the use of the Maxwell-Eucken equation in predicting thermal conductivity from water content are of particular interest. Surface film thermal resistance plays a very important role in heat transfer problems. The elementary data on surface film coefficients that have drawn up for food refrigeration leave room for substantial error in estimating rates of heat transfer and may account for some of the problems in food refrigeration process calculations.

SIMPLIFIED PREDICTION OF FREEZING AND THAWING TIMES OF FOODS. K. R. Scott and K. Hayakama, *ASHRAE Trans.* *83* (1), 541—548 (1977).

Methods of estimating freezing and thawing times are important in determining the design and operating regimes for processing plants in order to insure adequate product quality and achieve rated production throughout. A number of solutions have been proposed for various types of unsteady state conditions. They are idealized in that they do not take into account the inhomogeneous nature of foods or variations in thermal properties with temperature. The solutions also place various constraints on the form of the material and the freezing or thawing regime used. It is still useful, however, to use these idealized estimates since they show the effect on process times of changing various parameters and serve as a starting point for processing plant designs. Two of the easiest to use methods are Tao's charts and Plank's equation. These are described and examples given to illustrate their use.

ABSTRACTS FROM THE JOURNAL OF FOOD SCIENCE

Each of the following abstracts has been reprinted with permission from the *Journal of Food Science.*

DRUM DRYING FOR THE IMPROVED PRODUCTION OF INSTANT TORTILLA FLOUR. M. R. Molina, M. Letona and R. Bressani, Incap, *J. Food Sci. 42,* 1432—1434 (1977).

The present industrial production of tortilla flour is virtually an extrapolation of the home process, involving a cooking and drying operation as the main energy expenditures and costs. The possibility of preparing an acceptable instant tortilla flour, by means of other technologies, was therefore explored. Whole raw corn flour was mixed with water (ratio of 3:1) and lime (0.3% of the corn flour weight). This dough was then passed through a double-drum drier. With a drum opening of 0.003 in. (7.62×10^{-3} cm), it was found that the use of an internal pressure of either 15, 20 or 25 psig (93, 99 and 104°C surface temperature, respectively) at 2, 3 or 4 rpm, produced an instant tortilla flour with physico-chemical and organoleptic characteristics identical ($P < 0.05$) to those of the reference sample prepared by hand. In contrast, commercial samples of a similar product proved to be different ($P < 0.05$) from the standard and from the product obtained with the drum drier, both from the psysiochemical and organoleptic standpoints. Economically, the new process indicated that it was not only feasible, but that it also can allow for the supplementation of tortilla at the industrial level.

CONTINUOUS EXPLOSION-PUFFING OF POTATOES. J. F. Sullivan, R. P. Konstance, N. C. Aceto, W. K. Heiland and J. C. Craig Jr., *J. Food Sci. 42,* 1462—1463 (1977).

Scientists at Eastern Regional Research Center have successfully continuously explosion-puffed potatoes for dehydration. By using a newly designed and fabricated puffing unit, they demonstrated that this equipment can be used in a continuous explosion puffing system (CEPS). Equipment development was carried out to effect commercial reliability, acceptable products and a high output rate. Potato dice, 1.0 cm (3/8 in.) at 27% moisture were processed in CEPS at a maximum rate of 454 kg/hr (1000 lb/hr). With mechanical refinements largely complete, an optimization study was made. Using product rehydration and flavor as criteria, a puffing pressure of 345 kilo pascals (50 psig) at a moisture content of about 26% was optimal for the 1.0 cm dice.

BULK COMPRESSION TESTING OF PEACHES TO ASSESS TEXTURE. R. C. Clark and V. N. M. Rao, *J. Food Sci. 42,* 1478—1480 (1977).

Several varieties of fresh peaches at three maturity levels were subjected to bulk compression using a specially constructed apparatus. The texture notes of hardness, elasticity, graininess, and dry-moist mouthfeel were evaluated by a sensory panel. In an effort to determine if bulk compression may be used to evaluate texture in peaches a correlation analysis was performed on the instrumental and sensory data. It was found that hardness and elasticity were positively correlated with the bulk modulus and that the mouthfeel score showed a negative correlation with the modulus value.

PACKAGING SYSTEMS FOR TRANSPORT AND STORAGE OF LAMB. I. D. Tatum, G. C. Smith and Z. L. Carpenter, *J. Food Sci. 42*, 1517—1521 (1977).

Wholesale legs and loins were vacuum packaged, chilled with carbon dioxide (CO_2) pellets, or wrapped with polyvinyl chloride (PVC) film and transported-stored (0°C) for 7 or 14 days; intact carcases were unprotected or wrapped in PVC film and transported-stored for 7 or 14 days. Product was evaluated following transport-storage, during retail display and as cooked cuts. Vacuum packaged loins sustained less ($P < 0.05$) surface discoloration and had higher scores for muscle color and overall appearance than did loins chilled with CO_2 or loins wrapped in PVC film. Vacuum packaged legs had higher ($P < 0.05$) scores for appearance of subcutaneous fat and overall appearance than did legs chilled with CO_2 or legs wrapped in PVC film. Carcasses wrapped in PVC film had higher ($P < 0.05$) scores for appearance of subcutaneous fat and sustained less ($P < 0.05$) shrinkage during storage than did unprotected carcasses. Unprotected carcasses, however, had a lower incidence of off-odor. Carcasses or primal cuts which were transported-stored and placed in the retain case within 7 days were effectively protected from shrinkage and deterioration by wrapping with PVC film. Vacuum packaging was the only suitable means for protecting lamb and primal cuts during transport-storage intervals of 14 days.

INITIAL LOSSES OF AVAILABLE LYSINE IN MODEL SYSTEMS. J. C. Wolf, D. R. Thompson, and G. A. Reineccius, *J. Food Sci. 42*, 1540—1544 (1977).

The initial loss rates of available lysine during thermal processing were studied to develop an equation for predicting the specific reaction rate (k_T). The reaction order for initial loss was first determined and then the effect of system composition on the specific reaction rate investigated. The ability of the model system in phase three (no further loss with heating) to revert to phase one (initial loss rate) after mixing was also examined. A model system, consisting of protein, glucose and microcrystalline cellulose was utilized. The system composition (pH, water activity and glucose level) and time and temperature of the processing were varied. The reaction resulting in the initial rapid phase (one) of available lysine loss occurs according to first order reaction kinetics. Both pH and activity also influence the prediction of k_T but they act through an interaction with glucose. Once the soy based food system enters phase three, the system does not revert to phase one by the re-slurry method. Sugar exhaustion does not account for the inability to revert to phase one.

STUDIES ON THE COOKING RATE EQUATIONS OF RICE. K. Suzuki, M. Ari, K. Kubota and H . Hosaka, *J. Food Sci. 42*, 1545—1548 (1977).

The soaking and the cooking mechanisms of rice were investigated in terms of the mathematical rate equations in this study. The soaking and the cooking rate were measured by using the weighing method, and the soaking rate was examined at temperatures from 8 — 50°C, and the cooking rate from 70 — 98.5°C. The rate equation involved two rate parameters: the reaction rate parameter of the rice component with water and the diffusion rate parameter of water, was assumed. The results showed that the cooking rate was mainly limited by the reaction and the equivalent value of the activation energy of the reaction rate was nearly equal to 20 kcal/mol. though the cooking rate was relatively influenced by the diffusion rate of water in the cooked rice layer at 98.5°C. In the soaking of rice, the values of the diffusion rate parameter at from 8.0 — 50°C were smaller than the values at from 110—150°C.

ACCELERATED STABILITY TESTS OF MOISTURE-SENSITIVE PRODUCTS IN PERMEABLE PACKAGES AT HIGH RATES OF MOISTURE GAIN AND ELEVATED TEMPERATURES. S. Mizrahi and M. Karel, *J. Food Sci. 42*, 1575—1579 (1977).

The isothermal "no model" method of accelerated stability testing, which was developed for isothermal storage of moisture-sensitive dehydrated products packaged in water-vapor-permeable containers, was expanded to include storage at different temperatures. The expanded method can be applied to dehydrated products when moisture content changes continuously during storage and when rate of deterioration is only dependent on moisture content and temperature. Knowledge of how rate of deterioration depends on moisture is not required, but it is assumed that at each moisture level the temperature dependence is given by the Arrhenius equation. The method is based on accelerating the deterioration process by subjecting the product to high rates of moisture uptake at elevated temperatures. The mathematical procedure of predicting the extent of deterioration of any combination of package-storage conditions is based on a transformation of data to an arbitrarily determined reference moisture gain curve and an extrapolation to other temperatures by the Arrhenius equation. The method successfully predicted the loss of ascorbic acid in stored tomato powder and the extent of browning in dehydrated cabbage.

FIRMNESS OF CANNED CARROTS AND RED BEETS DURING STORAGE. S. Shannon, M. C. Bourne, and M. A. Rao. *J. Food Sci. 42*, 1675—1676 (1977).

Firmness of canned, diced carrots ('Royal Chantenay' and 'Spartan Fancy') and red beets ('Ruby Queen' and 'Detroit Dark Red') was measured by an extrusion method over a period of 600 days storage at 18°C and 38°C. There was a slight but significant increase in firmness of carrots during storage but no difference due to storage temperature. In contrast, there was a highly significant decrease in firmness of beets with storage time (860 Newtons to 660 Newtons) and the rate of loss in firmness was four times as rapid at 38°C as at 18°C. The rate of loss in firmness at 18°C was not sufficient to be detrimental to quality during normal holding periods. There were highly significant differences in firmness of cultivars of both crops.

FORCES INVOLVED IN PENETRATION TESTS OF CHEWING GUM. H. Bogaty, A. F. Rose and J. M. Talmage, *J. Food Sci. 42*, 1680—1682 (1977).

Penetration tests have been conducted on chewing gums of different ages and textures. Penetration forces were measured using 7 rods varying in diameter and at 2 testing speeds. The data were examined for fit to 2 different equations: (1) A model, previously given in the literature, which implies that the force of penetration is composed of shear components (proportional to rod diameter) and of compression components (proportional to the square of the rod diameter); (2) A model in which the penetration force consists of shear elements, as above, plus viscous components, proportional in this study to the 1.6th power of rod diameter. The observed data fit either model well; the equation postulating the presence of viscous deformation provides consistently, though not statistically, a superior fit. Penetration forces measured at low testing speed are consistently lower for corresponding samples and rods than those penetrated more rapidly, also suggestive of a viscosity component in the deformation process. The equation constants appear to be useful for characterizing chewing gum texture, responding sensibly to variations in the firmness of the material with age.

UNIT OPERATIONS FOR GENERATION OF INTACT OR UNIT KERNALS OF SWEET CORN. G. H. Robertson, M. E. Lazar, W. C. Galinat, D. F. Farkas and J. M. Krochta, *J. Food Sci. 42,* 1290—1293 (1977).

The mechanical removal of sweet-corn kernels from the cob by cutting or scraping leads to waste, loss of nutritional value, and loss of yield. Solutions to this problem are being developed by food engineers and plant breeders by modifying the mechanical separation method and by modifying the raw product processing characteristics. The goal of this work is to achieve the removal of intact kernels ("unit" kernels) from the cob. Preliminary tests comparing processing of conventional cut corn with unit kernel corn indicate the latter can result in a reduction in the effluent during washing (up to 80% reduction based on total carbon analysis) and water blanching (50% reduction), in increased yields which approach the total available edible portion (20% greater yield than cut corn on a per kernel basis), and in increased opportunity for in-field processing. Two mechanical techniques are under investigation. One of these employs a cutter which breaks away the kernel pedicel from presorted ears. A second removes kernels by applying a rubbing action to rows of kernels on ears which have been split lengthwise. Inherited modifications of the cob such as development of vestigial glume varieties with kernels that are easily detached from the cob may complement the improved technology for processing intact or unit kernel sweet corn.

✓ LOW TEMPERATURE AIR DRYING OF CARROT CUBES. F. W. Schmidt, Y. S. Chen, M. Kirby-Smith and J. H. MacNeil, *J. Food Sci. 42,* 1294—1298 (1977).

Individual frozen carrot cubes were suspended on wires and dried in a stream of low temperature dry air. One of the cubes was suspended on a thermocouple. During drying the weight and temperature of the product and the specific humidity, velocity and temperature of the air were recorded. An analytical model, utilizing the concept of external and internal resistances to the transfer of heat and mass, was developed for the prediction of the drying rate. The experimental data were used to determine a functional relationship between the internal resistances and the fraction of the original moisture remaining in the product. The drying rates predicted were in good agreement with experimental results.

ON THE EVALUATION OF B.E.T. CONSTANTS FROM THE B.E.T. ISOTHERM EQUATION. H. A. Iglesias, R. Boquet and J. Chirife, *J. Food Sci. 42,* 1387—1389 (1977).

It is shown that the conventional (or unweighed) least squares method must not be used to evaluate the B.E.T. constants, X_m and C, when using a rearranged linear B.E.T. plot recently suggested in the literature. This is illustrated using literature data on water sorption in several foods. In this case a semi-weighted (or weighted) least squares analysis becomes necessary. It is also shown that the unweighted least squares analysis should not be applied even to the familiar linear B.E.T. plot. In this particular case, however, and because of a fortuitous coincidence, this procedure leads to not significant differences — at least in food research — in the numerical values.

A COMPARISON OF ANALYTICAL AND NUMERICAL METHODS OF PREDICTING THE FREEZING TIMES OF FOODS. A. C. Cleland and R. L. Earle, *J. Food Sci. 42*, 1390—1395 (1977).

The problem of one-dimensional heat transfer in finite slabs of freezing food materials cooled from both sides is considered. The authors' modification to Plank's equation is compared with a numerical scheme. The paper shows that in the important slab freezing problem a simple formula, based on an approximate analytical solution, is at least as accurate as a complex finite difference formulation, and has some substantial practical advantages.

THE LETHALITY-FOURIER NUMBER METHOD: EXPERIMENTAL VERIFICATION OF A MODEL FOR CALCULATING TEMPERATURE PROFILES AND LETHALITY IN CONDUCTION-HEATING CANNED FOODS. M. K. Lenz and D. B. Lund, *J. Food Sci. 42*, 989—996 (1977).

A new method (lethality-Fourier number method) for calculating the center point sterilizing value of a thermal process applied to conduction-heating foods was developed by combining first-order destruction kinetics with the Arrhenius equation and dimensionalizing this equation. The temperature profile used in the Arrhenius equation is the theoretical center point temperature profile for heating and cooling of a finite cylinder. These temperature profiles were experimentally verified as adequate models. This verification procedure also produced estimates of the variation in the thermal properties or heating rates of conduction-heating foods. The final equation is numerically integrated to give charts of dimensionless lethality versus dimensionless time with dimensionless activation energy as a parameter. The method compares favorably with sterilizing values obtained from the Improved General Method and the Formula Method.

THE LETHALITY-FOURIER NUMBER METHOD: EXPERIMENTAL VERIFICATION OF A MODEL FOR CALCULATING AVERAGE QUALITY FACTOR RETENTION IN CONDUCTION-HEATING CANNED FOODS. M. K. Lunz and D. B. Lund, *J. Food Sci. 42*, 997—1001 (1977).

The lethality-Fourier number (L-τ) method (Lenz and Lund, JFS 42: 989, 1977) was extended so that mass-average retention of heat-labile quality factors (e.g., color and nutrients) could be calculated for conduction heating foods. The lethality number was volume-averaged for cylindrical containers for different Fourier heating times and dimensionless activation energies, generating average lethality number (L)-Fourier heating time (τ) charts. The method was evaluated by comparing predicted mass-average retention of thiamine and chlorophyll in food purees to those obtained experimentally. The method was also compared to several other methods which have been developed for calculating mass-average retention of heat-labile components. The results indicate that the L-τ method is at least as accurate as other available methods.

THE LETHALITY-FOURIER NUMBER METHOD: CONFIDENCE INTERVALS FOR CALCULATED LETHALITY AND MASS-AVERAGE RETENTION OF CONDUCTION-HEATING, CANNED FOODS. M. K. Lenz and D. B. Lund, *J. Food Sci. 42*, 1002—1007 (1977).

The accuracy associated with a calculated lethality or mass-average retention is dependent on the accuracy of the variables needed for the calculation. This study was undertaken to determine the effect of biological variability in destruction rates of microorganisms and quality factors and in thermal diffusivity on accuracy of thermal process calculations. Estimates of the distributions of these biological parameters were used in a Monte Carlo procedure to generate distributions of calculated lethality and mass-average retention. From these distributions, the error in thermal process calculations could be determined. Variation in parameters describing destruction rates and thermal diffusivity of the food can result in standard deviation for the F-value of 10—15% of the F-value at small Fourier numbers (dimensionless heating time). At larger Fourier numbers ($\geqslant 0.7$) the standard deviation is approximately 5—8%. For mass-average retention, the maximum standard deviation is approximately 5%.

SHEAR EFFECTS ON CELL VIABILITY DURING EXTRUSION OF SEMI-MOIST FOODS. K. B. Kauffman and R. T. Hatch, *J. Food Sci. 42*, 906—910 (1977).

The effect of shear on yeast viability in semi-moist dogfood was examined using a Brabender extruder. It was found that the viability of yeast cells could be reduced by 20—60% at 40°C by single pass extrusion through 3.18 mm bore tubes of 2.5—30.5 cm lengths. Auger speeds of 20—50 rpm resulted in mass flowrates of 6.7—19.6 g/min. A semi-empirical rate equation was developed to relate the shear rate, fluid behavior, and residence time to cell viability. Regression analysis showed a linear dependency of log decimal cell viability on the power input per food mass in the shear zone of the extruder die.

FREEZING OF VEGETABLES BY DIRECT CONTACT WITH AQUEOUS SOLUTIONS OF ETHANOL AND SODIUM CHLORIDE, J. C. Cipoletti, G. H. Robertson, and D. F. Farkas, *J. Food Sci. 42*, 911—916 (1977).

Aqueous freezant (AF 15-15) consisting of 15% NaCl and 15% ethanol with a —19.3°F solubility limit was developed for direct contact freezing of vegetables. Carrots (3/8 in dice) and peas were frozen and cooled to 2.5°F in 1.5 min of immersion and beans (1 in cut) and whole kernel corn were frozen and cooled to 2.5° in 2.5 min of immersion. AF 15-15 frozen and blotted peas, beans and corn contained 0.72—0.82% NaCl and were statisticaly indistinguishable from air-blast frozen vegetables in organoleptic ratings. Air-blast frozen carrot dice were preferred over AF frozen dice which contained 1.77% NaCl. A mixture of all of the above vegetables frozen in AF 15-15 was slightly favored over an air-blast frozen mixture (6.7 vs 5.8 score). AF frozen vegetables showed a small (2.3—0.9%) weight gain, whereas the air-blast frozen vegetables showed losses of from 3.9—13.3% with respect to fresh weight.

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HASSON, E. P. and LATIES, G. G. 1976. Separation and characterization of potato lipid acylhydrolases. Plant Physiol. *57*, 142–147.

ZABORSKY, O. 1973. *Immobilized Enzymes*, pp. 28–46, CRC Press, Cleveland, Ohio.

Journal abbreviations should follow those used in *Chemical Abstracts*. Responsibility for the accuracy of citations rests entirely with the author(s). References to papers in press should indicate the name of the journal and should only be used for papers that have been accepted for publication. Submitted papers should be referred to by such terms as "unpublished observations" or "private communication." However, these last should be used only when absolutely necessary.

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