NP

JOURNAL OF FOOD PROCESSING AND PRESERVATION

D.B. LUND
EDITOR

FOOD & NUTRITION
PRESS, INC.

VOLUME 19, NUMBER 6

DECEMBER 1995

JOURNAL OF FOOD PROCESSING AND PRESERVATION

All articles for publication and inquiries regarding publication should be sent to Dr. D.B Lund, Dean of Agriculture and Life Sciences, Cornell University, 260 Roberts Hall, Ithaca, New York 14853-4203 USA. There are no page charges for publication in the *Journal of Food Processing and Preservation.*

All subscriptions and inquiries regarding subscriptions should be sent to Food & Nutrition Press, Inc., 6527 Main Street, P.O. Box 374, Trumbull, CT 06611 USA.

One volume of four issues will be published annually. The price for Volume 19 is $150.00, which includes postage to U.S., Canada, and Mexico. Subscriptions to other countries are $170.00 per year via surface mail, and $181.00 per year via airmail.

Subscriptions for individuals for their own personal use are $120.00 for Volume 19, which includes postage to U.S., Canada, and Mexico. Personal subscriptions to other countries are $140.00 per year via surface mail, and $151.00 per year via airmail. Subscriptions for individuals should be sent directly to the publisher and marked for personal use.

The *Journal of Food Processing and Preservation* is listed in *Current Contents/Agriculture, Biology & Environmental Sciences (CC/AB).*

The *Journal of Food Processing and Preservation* (ISSN:0145-8892) is published bimonthly by Food & Nutrition Press, Inc.—Office of Publication is 6527 Main Street, P.O. Box 374, Trumbull, Connecticut 06611 USA.

Second class postage paid at Bridgeport, CT 06602.

POSTMASTER: Send address changes to Food & Nutrition Press, Inc., 6527 Main Street, P.O. Box 374, Trumbull, Connecticut 06611 USA.

JOURNAL OF FOOD PROCESSING AND PRESERVATION

JOURNAL OF FOOD PROCESSING AND PRESERVATION

Editor: **D.B. LUND**, Dean of Agriculture and Life Sciences, Cornell University, 260 Roberts Hall, Ithaca, New York

Editorial Board: **W. BREENE**, Department of Food Science and Nutrition, University of Minnesota, St. Paul, Minnesota

F.F. BUSTA, Department of Food Science and Nutrition, University of Minnesota, St. Paul, Minnesota

J.J. CASH, Department of Food Science and Human Nutrition, Michigan State University, East Lansing, Michigan

O. FENNEMA, Department of Food Science, University of Wisconsin, Madison, Wisconsin

M. KAREL, Department of Food Science, Rutgers, The State University, Cook College, New Brunswick, New Jersey

T.P. LABUZA, Department of Food Science and Nutrition, University of Minnesota, St. Paul, Minnesota

L. SATTERLEE, College of Agriculture, North Dakota State University, Fargo, North Dakota

B.G. SWANSON, Food Science and Human Nutrition, Washington State University, Pullman, Washington

K.R. SWARTZEL, Department of Food Science, North Carolina State University, Raleigh, North Carolina

R.T. TOLEDO, Department of Food Science, Unviersity of Georgia, Athens, Georgia

J.H. VON ELBE, Department of Food Science, University of Wisconsin, Madison, Wisconsin

R. WROLSTAD, Department of Food Technology and Chemistry, Orgeon State University, Corvallis, Oregon

Journal of FOOD PROCESSING and PRESERVATION

VOLUME 19
NUMBER 6

Editor: D.B. LUND

FOOD & NUTRITION PRESS, INC.
TRUMBULL, CONNECTICUT 06611 USA

Food & Nutrition Press, Inc.
Trumbull, Connecticut 06611 USA

ISSN 0145-8892

Printed in the United States of America

CONTENTS

EXTRACTION OF MILK FAT IN HIGH PRESSURE SOLVENTS

YEN-CHUN WANG[1], RICHARD W. HARTEL[1,4], JUNGRO YOON[2]
and R. SELWYN JEBSON[3]

[1]*Department of Food Science*
University of Wisconsin-Madison
1605 Linden Drive
Madison, WI 53706

[2]*Department of Food Science*
Kangnung National University
Chibyun-Dong
Kangnung, Kangwon-Do, South Korea

[3]*Department of Food Technology*
Massey University
Palmerston North, New Zealand

Accepted for Publication July 31, 1995

ABSTRACT

Extraction of milk fat in several high pressure solvents was compared. Solubility of milk fat in supercritical (SC) ethylene and liquid propane was compared to previous results in SC CO_2. At the same operating conditions (temperature and pressure), solubility of milk fat was higher in SC ethylene than in CO_2, although levels generally remained below 5% (w/w). This resulted in significantly higher solubility in SC ethylene when compared at equivalent solvent density. Very little fractionation of milk fat occurred in liquid propane over the range of pressures (3.45 to 5.52 MPa) and temperatures (30 to 90C) studied. Below 77.5C and 2.76 MPa, liquid propane and milk fat were miscible, while a slight fractionation was observed above these conditions. A high pressure sight-gage apparatus was used to visually confirm these conditions for separation.

---

[4]To whom correspondence should be addressed; Ph: (608)263-1965, FAX (608)262-6872, Email: hartel@calshp.cals.wisc.edu.

Journal of Food Processing and Preservation **19**(1995) 409–425. *All Rights Reserved*

INTRODUCTION

One potential technique to increase utilization of milk fat in many food applications involves separation of milk fat into various fractions with distinct physical and chemical properties. Several fractionation techniques have been studied over the past decades, including solvent fractionation (Norris *et al.* 1971; Schaap *et al.* 1975; Antila 1979), melt crystallization (deMan and Finoro 1980; Badings *et al.* 1983; Amer *et al.* 1985; Deffense 1987; Fouad *et al.* 1990), detergent fractionation (Fjaervol 1970; Jebson 1970, 1974), short path distillation (Arul *et al.* 1988) and supercritical fluid extraction (Arul *et al.* 1987; Rizvi *et al.* 1989; Hammam *et al.* 1991; Chen *et al.* 1992; Yoon *et al.* 1993; Bhaskar *et al.* 1994).

High pressure solvents have received increasing attention in recent years as a potential alternative for lipid separations. The attractions of high pressure solvent extraction for many applications include (1) better extraction and separation of hard-to-fractionate systems, (2) pollution-free operation, (3) high purity end-products, (4) low temperature operation, (5) utilization of an inert solvent, and (6) possibility of tailored separations based on control of temperature and pressure. Among possibilities for high pressure solvents, supercritical (SC) CO_2 has received the most attention due to its nontoxicity, nonflammability and low to moderate operating conditions. The critical point for CO_2 is 304.2K and 7.38 MPa with a density at the critical point of 0.468 g/cm^3 (Rizvi *et al.* 1986).

Another potential high pressure solvent is SC ethylene (Kurnik *et al.* 1981; Najour *et al.* 1966; Tsekhanskaya *et al.* 1964) since it is also nontoxic and recyclable, and has reasonably low critical point (Tc = 282.4K and Pc = 5.03 MPa). It has been shown to have enhanced solvent power for naphthalene under supercritical conditions (McHugh and Krukonis 1986). However, its major drawback for use in the food industry is safety, due to its high flammability. In addition, there has been no research in the area of extraction of lipids with SC ethylene.

Propane is an odorless gas at standard temperature and pressure, but can be readily liquified by compression. It is stable, nonpolar, noncorrosive and inexpensive. Compared to CO_2, propane has a critical point (Tc = 369.8K and Pc = 4.24 MPa) at conditions where most lipids are oils of increased volatility, and the chemical structure of propane is more similar to oils. With these advantages, liquid propane has been advocated for refining fatty oils (Ewing 1935).

Liquid propane has been used to fractionate lipid materials, as described by the Solexol process (Passino 1949), which has been used for extraction of animal, vegetable and marine oils. Liquid propane has also been used to process lubrication oils (Bray *et al.* 1934), extract fatty acids and esters (Hixson and

Hixson 1941; Drew and Hixson 1944), refine fatty oils (Mattikow 1950), and for processing heavy oils (Wilson *et al.* 1936). Recently, several researchers have been studying the solubilities of fatty acids and triglycerides in liquid propane (Coorens *et al.* 1988; Straver *et al.* 1991; Straver *et al.* 1993) and have demonstrated the possibility of separating lipid components according to their chain length and, to some extent, degree of saturation. However, liquid propane has never been tested for fractionation of milk fat. If successful, liquid propane might provide a more economical method of fractionating milk fat, as compared to SC CO_2.

The focus of this research was to study the solubility and selectivity of milk fat in several high pressure solvents, for comparison with SC CO_2. The feasibility of extracting and fractionating milk fat in alternative solvents was explored in this way.

MATERIALS AND METHODS

Column Extractor

A packed bed, column extractor, similar to that used by Yoon *et al.* (1993), was used for both SC ethylene and liquid propane extraction. A general schematic of the extraction apparatus is shown in Figure 1. A 500 ml surge tank was used to dampen out pressure fluctuations as high pressure solvent was pumped into a 500 ml extraction vessel (5 cm ID, 24 cm height). Two heated, micrometering valves were connected to the outlet of the extractor to control flow rate during extraction.

High pressure was attained using an air-driven liquid pump (Newport Scientific, Jessup, MD) for both liquid propane and SC ethylene. A pressure regulator (Dynareg, Circle Seal Controls, Anaheim, CA) was installed between surge vessel and extractor to control pressure during extraction. Typically, pressure in the extractor was maintained within 10 kPa. Two pressure transducers (model Ashcroft K1, Dresser Industries, Stratford, CT) were mounted at the inlet and outlet of the extraction column, in addition to a pressure gage attached to the surge vessel. The transducers were interfaced with a microcomputer (Zenith Data Systems, St. Joseph, MI) and pressure readings collected through Labtech Notebook software (Labtech, Willmington, MA). During sample collection, the flow rate and total volume of solvent were measured by mass flow meter and totalizer (Omega Engineering, Stanford, CT), respectively.

The surge vessel was heated using a constant temperature water bath, maintained by a precision temperature controller (Bayley Instrument Co.,

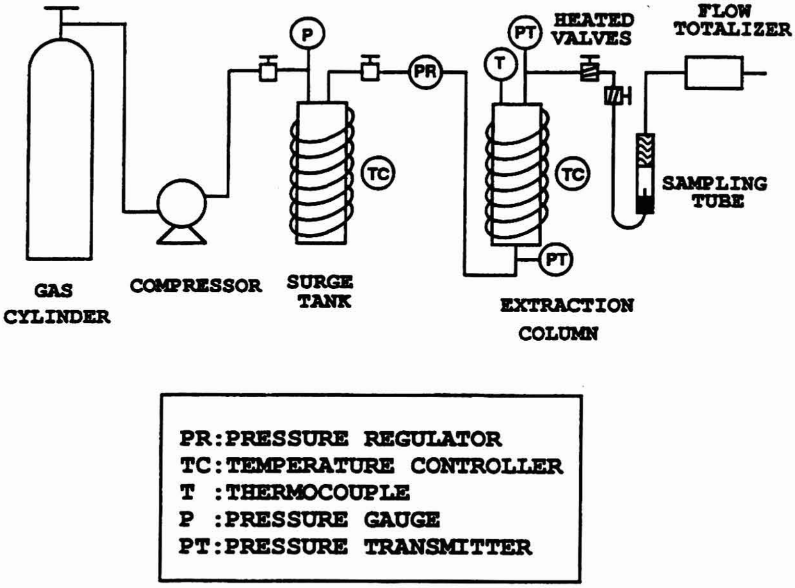


FIG. 1. SCHEMATIC OF EXTRACTION APPARATUS.

Kenwood, CA). A heavy duty, silicone rubber, spark-proof heating tape (Barnstead/Thermolyne, Dubuque, IA) was used to maintain temperature (within 0.1C) in the extraction vessel. A thermocouple (TQSS-14G-b, Omega Engineering, Stanford, CT) inserted into the extraction vessel was used to monitor and control extractor temperature. The extraction system was mounted inside a laboratory hood with all control units placed outside the hood, for safety concerns. Solvent concentration in the air was monitored at all times by a combustible gas leak detector (Sierra Monitor Corp., Chicago, IL).

Anhydrous milk fat (AMF) with water content less than 0.5% was obtained from Level Valley Dairy, West Bend, WI. Ethylene (99.5%) and propane (99.9%), both from Liquid Carbonic, Chicago, IL, were used directly from the canisters. All other chemicals used were reagent grade.

Sight Gage Apparatus

For visual observation of phase behavior between liquid propane and milk fat, a sight gage apparatus was constructed. This system was similar to the previous extraction column system, with a sight gage replacing the extraction column. A high pressure sight gage (EWT-15-6, Ernst Gage Co., Livingston, NJ) was modified to allow connection of high pressure tubing. A larger surge vessel (1200 mL) was used in place of the 500 ml tank, to allow a larger reservoir of high pressure solvent. Temperature was controlled by immersing the surge tank and sight gage in a large water bath, with temperature controlled by the precision controller.

Operation and Sampling

Column Extraction Experiments. Milk fat was coated evenly on glass beads (0.5 mm OD) by mixing liquified milk fat with beads at a weight ratio of 1:38. This gave an average milk fat thickness of 0.11 mm. The coated beads were then packed into the extractor, with a total loading of between 17-19 g. The bottom and top of the extractor were filled with a 2 cm layer of glass wool. In order to minimize intermixing of glass beads, and facilitate measurement of break-through curves, the beads were packed into five sections, separated by a 1 mm layer of glass wool. The reactor was sealed and air purged from the system by flushing with solvent for five minutes. After venting, the vessels were heated and pressurized to the desired conditions. For SC ethylene, temperatures were varied from 40 to 60C and pressure from 15.0 to 25.0 MPa. For liquid propane, extractions were conducted at 30 to 90C and 3.45 to 5.52 MPa. All experiments were conducted in duplicate.

The system was held at set temperature and pressure for at least two hours to ensure equilibrium between milk fat and solvent. During sampling, saturated solvent was exhausted from the top of the extractor and fresh solvent from the surge vessel was fed to the bottom. Slow solvent flow rates, between 0.5 to 6 L/min (at atmospheric pressure and 25C), were used during sampling to maintain equilibrium extraction conditions. Samples were collected under continuous flow in a sample collector made of tygon tubing (150 cm long) and a plastic sample tube (30 ml) packed with glass wool. This allowed all extracted lipid material to be collected after depressurization of solvent. Solvent was vented through a heated micrometering valve into the sample tube, and remaining solvent was passed through the mass flow meter and totalizer for flow rate and total volume, respectively. The material collected in the sample tubes was weighed and concentrations calculated based on the weight of solvent for each fraction.

Sight Gage Experiments. About 27 g of milk fat was loaded into the sight gage apparatus (volume approximately 100 ml) for visual observation of phase behavior between liquid propane and milk fat. The sight gage was sealed, flushed with propane, submerged in the water bath and allowed to equilibrate at system temperature. Liquid propane from the reservoir (holding propane pressure of 20.0 MPa) was rapidly introduced into the sight gage to induce good mixing with the liquid milk fat. The sight gage pressure was set at 6.9 MPa by adjustment of the pressure regulator. At this condition, milk fat and liquid propane were totally miscible at all temperatures. After 30 min, the sight gage was depressurized at a rate of 3-5 kPa/min at constant temperature. The phase condition was monitored visually through the window of the gage using a flash light and mirror. The pressure was recorded when a phase change was first observed. The system was then maintained at that pressure for at least 20 min to allow complete phase separation. The temperature was increased in 5C increments and the procedure repeated between 30 and 70C. Between 70 and 90C, temperature increments of 2.5C were used. In one study, the effect of milk fat to propane level was evaluated by using half the initial amount of milk fat (13.5 g) under the same conditions.

Milk fat samples from the top liquid (propane rich) phase were taken for analysis after a phase separation was observed. A sample collection tube was connected to the outlet valve from the top of the sight gage and solvent flow rate was kept below 500 ml/min (at 1 atmospheric pressure and 25C). During sampling, the pressure in the sight gage was maintained constant by control of the pressure regulator. Sampling conditions chosen were between 78 and 85C and 3.45 to 5.51 MPa (500-800 psi), since this was the region of two liquid phase behavior.

Sample Analysis

Thermal Profiles. A Perkin Elmer DSC 7 (Norwalk, CT) differential scanning calorimeter with a liquid nitrogen reservoir was used to measure melting and cooling curves of milk fat fractions. Indium and mercury were used for a two-point calibration, with melting points at −38 and 156C, respectively. The sample chamber was continually purged with helium at 0.14 MPa. The sample pan, containing 7-11 mg of lipid, was placed in the chamber at 25C and heated to 60C. After a 5-min hold, the sample was cooled to 30C at 10C/min, held for 1 min and warmed to 60C at 10C/min to give cooling and melting curves, respectively.

Triglyceride Analysis. The triglyceride composition (acyl carbon number) of all milk fat samples was determined by Gas Chromatography (GC) utilizing a modified method of Lund (1988). Samples were prepared by dissolving 6 mg of lipid in 1 ml isooctane which contained 0.1 mg trinanoin as an internal standard. A Varian 3700 GC (Varian Association, Palo Alto, CA) equipped with a flame ionization detector (FID) and on-column injector was used. The column was a 25 m by 0.25 mm, WCOT triacylglycerol analysis phase, stainless steel capillary (Chrompack, Raritan, NJ). Carrier gas was pure helium at a flow of 2 ml/min. Pure hydrogen and air were supplied to the FID at all times. One μl of sample was injected and the temperature program for triglyceride separation was as follows: 1 min hold at 220C after injection followed by an increase to 335C at 3C/min. Data was collected and processed by a NEC Powermate SX Plus computer (NEC, Boxborough, MA) operating Baseline 810 chromatography software (Dynamic Solutions, Ventura, CA). Concentrations were calculated as standard weight percent.

Fatty Acid Analysis. Fatty acid composition of milk fat samples was determined by GC after conversion to fatty acid butyl ester derivatives according to a modified method of Iverson and Sheppard (1968). Samples were injected into a Tracor 560 GC (Tracor, Burbank, CA) equipped with a FID and a glass column (1/8 in. ID by 6 ft length) packed with GP 10% SP-2330 on 100/120 Chromosob WAW (Supelco, Bellefonte, PA). The carrier gas was pure nitrogen at 10 ml/min (0.28 MPa). The column oven temperature was programmed as follows: hold at 75C for 5 min., increase to 220C at a rate of 8C/min and hold at 220C for 15 min. Injector and detector temperatures were 250 and 225C, respectively. Peak areas were integrated by a Spectra Physics (model SP4270) integrator and concentration of each ester calculated in weight percent relative to the internal standard (nonanoic acid).

RESULTS AND DISCUSSION

Extraction Column

Extraction curves showing amount of oil extracted as a function of cumulative amount of solvent passed through the column are shown in Fig. 2 and 3 for SC ethylene and liquid propane, respectively. The shape of the extraction curves is generally the same for both solvents. After an initial lag period where very little milk fat was extracted, the rate of extraction (slope) of milk fat became linear and then gradually decreased with time as the more soluble components were depleted. Such extraction behavior has been previously observed (Yoon *et al.* 1993; Rizvi *et al.* 1989; Shishikura *et al.* 1986) for milk fat extraction in SC CO_2.

The initial lag period in the extraction curves (Fig. 2 and 3) is explained as follows. As liquid propane was filled into the extraction column, a slight depressurization occurred as the propane expanded to fill the column. About

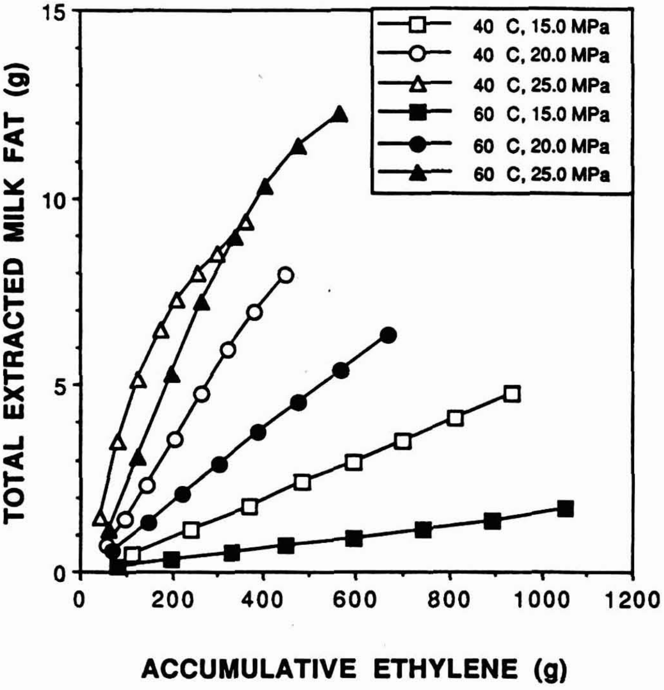


FIG. 2. EXTRACTION CURVES FOR SUPERCRITICAL ETHYLENE EXTRACTION OF MILK FAT

20 ml expanded propane filled the tubing, after the column, leading to the micrometering valve, and did not contact milk fat under experimental conditions. This propane was also the first to exit the extraction system, and carried little solubilized milk fat, resulting in an initial lag period.

A solubility value was calculated from the initial linear slope of the extraction curves. For SC ethylene, these solubilities were compared to those found for SC CO_2 from Yoon *et al.* (1993) in Fig. 4 and 5. From Fig. 4, the solubility of milk fat in SC ethylene was generally higher than in SC CO_2 at equivalent pressures and temperatures. This trend was more pronounced at higher pressures. Note that solubility of milk fat in SC ethylene was higher at 40C than at 60C at equivalent pressure. Similar behavior was found previously for SC CO_2 (Yoon *et al.* 1993). When solubilities are compared at equivalent density, slightly different behavior was observed (Fig. 5). Despite the lower density of SC ethylene as compared to SC CO_2, the solubility of milk fat in ethylene was significantly higher. Thus, ethylene shows an enhanced solvent

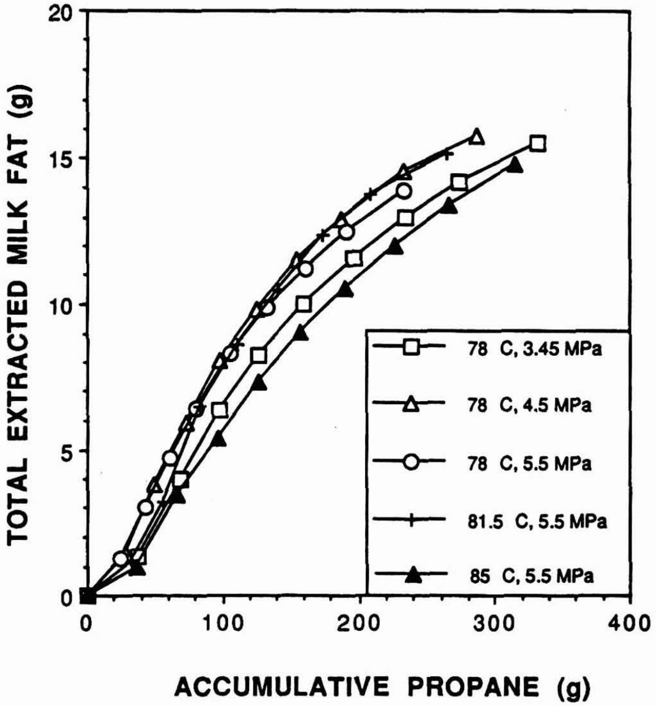


FIG. 3. EXTRACTION CURVES FOR LIQUID PROPANE EXTRACTION OF MILK FAT

power for milk fat triglycerides as compared to CO_2. Although both solvents are nonpolar, ethylene has a more similar chemical structure to triglycerides than does CO_2. Therefore, the higher solubility of milk fat in ethylene was expected.

The solubility of milk fat in liquid propane between 3.45 MPa (500 psi) and 5.51 MPa (800 psi), at 78C, was found to be between 9 to 10% (w/w), with no dependence on pressure. In addition, at 5.51 MPa, no effect of solubility on temperature between 78 and 85C was found. At temperatures below 78C, milk fat removed from the extractor in the propane stream showed no evidence of fractionation. Milk fat removed with propane (at temperature less than 78C) had identical physical and thermal properties (based on visual observation and DSC data) as the original milk fat loaded into the extractor. It was concluded that milk fat and liquid propane were completely miscible at these conditions. When temperature was raised above 78C, fractionation occurred, and the extraction curves shown in Fig. 3 were obtained.

The solubility of milk fat in liquid propane, above 78C and 3.45 Mpa (500 psi), was not a function of either temperature or pressure. Within experimental error, there was no difference in solubility of milk fat in liquid propane under

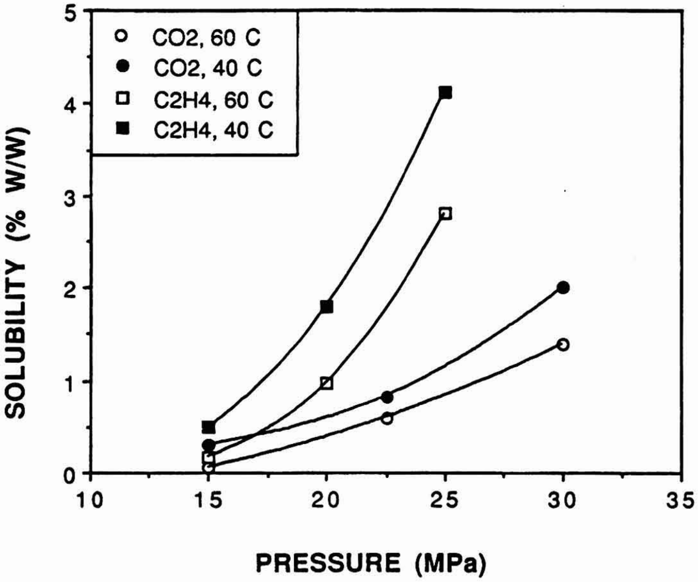


FIG. 4. SOLUBILITY OF MILK FAT IN SUPERCRITICAL ETHYLENE AND CO_2 AS A FUNCTION OF TEMPERATURE AND PRESSURE
Results for CO_2 from Yoon *et al.* (1993)

these conditions, although the temperature range studied was quite small. The amount of milk fat solubilized with liquid propane was considerably higher even than for SC ethylene and significantly higher than for SC CO_2. In terms of molecular structure, lipids are more similar to propane than to either ethylene or CO_2, resulting in this enhanced solubility. However, along with this enhanced solubility goes more limited fractionation.

DSC cooling curves demonstrate the fractionation capacity of SC ethylene and liquid propane. Typical cooling curves for SC ethylene and liquid propane are shown in Fig. 6 and 7, respectively. The fractions removed earliest from the column (fractions 1-3) contain significantly less of the high-melting components of milk fat, as seen by reduction in the crystallization peak at about 14C in the original milk fat. Fractions removed later in the process have cooling curves that are shifted to higher temperatures, since they are more concentrated in these high-melting components. The residual fat remaining in the column after extraction is significantly depleted in the lower-melting components, resulting in initial crystallization during cooling at about 23C for the ethylene fractions.

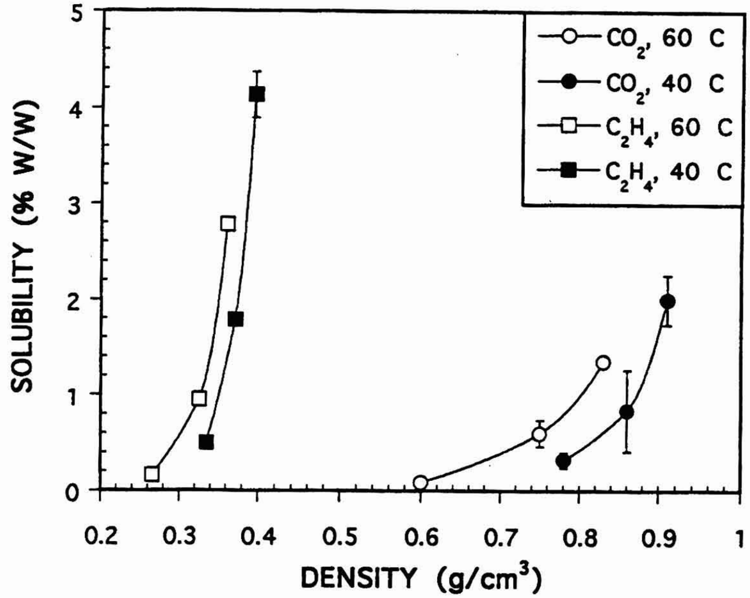


FIG. 5. SOLUBILITY OF MILK FAT IN SUPERCRITICAL ETHYLENE AND CO_2 AS A FUNCTION OF SOLVENT DENSITY
Results for CO_2 from Yoon *et al.* (1993)

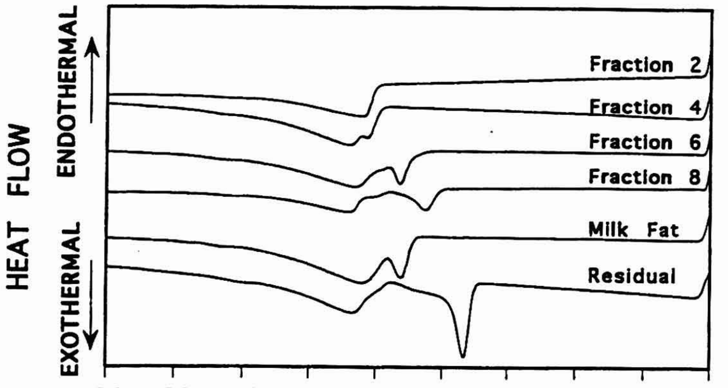


FIG. 6. DSC SOLIDIFICATION CURVES FOR MILK FAT FRACTIONS OBTAINED BY SUPERCRITICAL ETHYLENE EXTRACTION AT 40C AND 1.5 MPA

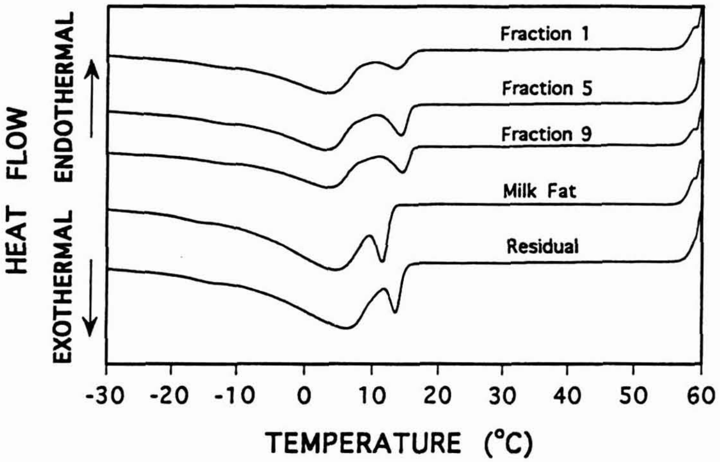


FIG. 7. DSC SOLIDIFICATION CURVES FOR MILK FAT FRACTIONS OBTAINED BY LIQUID PROPANE EXTRACTION AT 78C AND 5.51 MPA (800 PSI)

This behavior has been well-documented for fractionation of milk fat in SC CO_2 (Yoon *et al.* 1993). Comparing Fig. 6 and 7 clearly shows the lack of fractionation capability of liquid propane for milk fat, over the range of conditions studied. Although the amount of milk fat extracted in liquid propane was higher than for SC ethylene, the degree of fractionation was much reduced. The differences observed in Fig. 7 do not translate into significant visual differences in these fractions, as each of these fractions or residual appeared quite similar in physical properties to the original AMF.

In the range of temperature and pressure studied, fractionation of triglycerides and fatty acids in SC ethylene and liquid propane followed the expected trends, based on the DSC curves. Similar results have been shown previously for fractionation of milk fat in SC CO_2 (Yoon *et al.* 1993). The first fractions removed from the column, which were made up primarily of low melting components of milk fat, were enriched in lower acyl carbon number (shorter) triglycerides and depleted in the higher acyl carbon number triglycerides. This trend was reversed for the later fractions and the residual left in the extractor. The acyl carbon number curves crossed for these different fractions at about an acyl carbon number of 42, similar to that for extraction in SC CO_2. In terms of fatty acid composition, the first fractions removed were enriched in 4:0 to 14:0

fatty acids and depleted in 16:0 and 18:0 saturated fatty acids. The reverse trend was again true for the later fractions and the residual. The unsaturated fatty acids (18:1 and 18:2) were also primarily retained in the later fractions and residual, similar to previous results using SC CO_2 (Kankare *et al.* 1989; Hammam *et al.* 1991). SC ethylene also primarily separates fatty acids based on molecular size and not based on functionality (saturation).

Sight Gage Apparatus

In order to verify the results for liquid propane, a sight gage apparatus was used to visually determine phase separation boundaries between milk fat and liquid propane. At temperatures below 78C, the only phase boundary observed was the onset of propane vapor formation as the pressure was reduced to the bubble point. At higher pressures, only a single liquid phase was observed. When temperature was above 78C and pressure lowered from 6.9 MPa, a point was reached where two liquid phases became evident. At first, the solution became cloudy as the two liquids were separating. After about 20 min at constant conditions, a phase boundary separating two clear liquids was evident. The top portion was enriched in liquid propane while the bottom portion was enriched in milk fat. Note that this critical point of about 78C corresponds to conditions where fractionation occurred in the column extractor, verifying the earlier results. These experiments were repeated several times, and the phase boundaries visually determined were within a few percent each time. The effect of composition (milk fat to propane ratio) was also investigated. There was no apparent effect on these phase boundaries when the milk fat content was reduced by one-half. Thus, the composition did not have an effect on these phase boundaries over the range of conditions studied.

Samples were carefully taken from the top liquid (propane enriched) portion of the sight gage for analysis. A solubility measurement was made by weighing the amount of milk fat fraction separated with a measured quantity of propane. Samples were removed slowly so as not to disturb the phase equilibrium. The solubility measured in the sight gage apparatus was nearly twice that measured using the column extractor. Solubilities of nearly 20% (w/w) were observed, although there was still no dependence on pressure or temperature in this narrow range. The reason for this difference between measuring techniques was most likely due to mixing problems in the liquid column extractor for liquid propane conditions and subsequent carryover of liquid milk fat into the propane. At 78-85C, the milk fat was no longer stable on the glass beads and flowed to the bottom of the extractor. As liquid propane was passed upwards through the column, there was only a small layer of milk fat for contact at the bottom of the extractor and equilibrium conditions were not attained. This was verified both visually after completion of an extraction and by DSC curves of samples taken from several points in the column. Thus, we feel that the true solubility of milk fat in liquid propane is indeed the higher value, with upwards of 20% milk fat solubilized at these temperatures and pressures. Again, below this critical point (78C), no liquid phase separation was observed at any pressure. Note that mixing problems in column extraction of milk fat using SC ethylene were not observed due to lower temperature conditions used and better separation between liquid milk fat and the supercritical fluid.

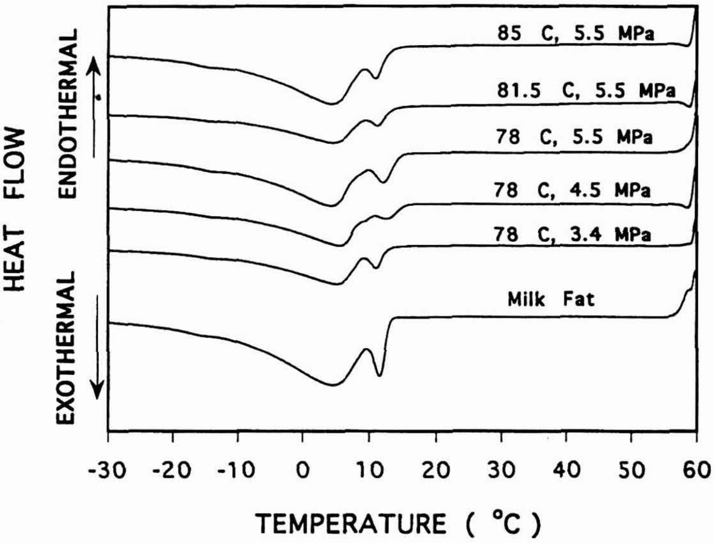


FIG. 8. DSC SOLIDIFICATION CURVES FOR MILK FAT FRACTIONS OBTAINED FROM LIQUID PROPANE EXTRACTION IN THE SIGHT GAGE APPARATUS

Samples removed from the light liquid layer (top) from the sight gage apparatus were analyzed for DSC cooling curve, and triglyceride and fatty acid composition. DSC cooling curves again show that there is some fractionation of milk fat, where the fractions contain slightly less of the high-melting component of AMF. There was some small effect of different temperature and pressure conditions, as seen in Fig. 8. However, any differences were quite small. The same differences were found for fractions produced in the packed column extractor at similar conditions. GC analysis verified triglyceride and fatty acid composition results. Again, the extracted fractions were enriched in lower acyl carbon number triglycerides (below about 42) and enriched in higher acyl carbon number triglycerides (above about 42). Very little effect of temperature and pressure were observed, probably due to the narrow range of conditions studied. Fatty acid profiles showed only small differences from the original AMF, with the extracted fractions being enriched slightly in shorter chain fatty acids and depleted in longer chain fatty acids. Again, the extracted fractions were slightly reduced in the unsaturated fatty acids, although very little difference was observed.

From these results, it can be concluded that SC ethylene gives slightly greater extraction of milk fat than SC CO_2 over the temperature and pressure ranges studied. In addition, liquid propane, while exhibiting greater solvent power than either SC ethylene or CO_2, was less able to fractionate milk fat into high and low melting components.

ACKNOWLEDGMENTS

Funding for this project was provided by the Wisconsin Milk Marketing Board and the New Zealand Dairy Board by a grant through the Wisconsin Center for Dairy Research.

REFERENCES

AMER, M.A., KUPRANYCZ, D.B. and BAKER, B.E. 1985. Physical and chemical characteristics of butterfat fractions obtained by crystallization from molten fat. J. Amer. Oil Chem. Soc. *62*, 1551–1557.

ANTILA, V. 1979. The fractionation of milk fat. Milk Industry. *81*, 17–20.

ARUL, J., BOUDREAU, A., MAKHLOUF, J., TARDIF, R. and SAHASRABUDHE, M. 1987. Fractionation of anhydrous milk fat by supercritical carbon dioxide. J. Food Sci. *52*(5), 1231–1236.

ARUL, J., BOUDREAU, A., MAKHLOUF, J., TARDIF, R. and BELLAVIA, T. 1988. Fractionation of anhydrous milk fat by short-path distillation. J. Amer. Oil Chem. Soc. *65*(10), 1642–1646.

BADINGS, H.T., SCHAAP, J.E., DEJONG, C. and HAGEDOORN, H.G. 1983. Analytical study of fractions obtained from stepwise cooling of melted milk fat. 1. Methodology. Milchwissenschaft. *38*, 95–97.

BHASKAR, A.R., RIZVI, S.S.H. and HARRIOTT, P. 1993. Performance of a packed column for continuous supercritical carbon dioxide processing of anhydrous milk fat. Biotech. Prog. *9*, 70–74.

BRAY, U.B., SWIFT, C.E. and CARR, D. 1934. Use of propane in lube oil refining. Refiner and Natural Gas Manuf. September, 333.

CHEN, H., SCHWARTZ, S.J. and SPANOS, G.A. 1992. Fractionation of butter oil by supercritical carbon dioxide. J. Dairy Sci. *75*, 2659–2669.

COORENS, H.G.A., PETER, C.J. and SWAAN ARONS, J. de. 1988. Phase equilibria in binary mixtures of propane and tripalmitin. Fluid Phase Equilibria. *40*, 135–151.

DEFFENSE, E. 1987. Multi-step butteroil fractionation and spreadable butter. Fette Wissenschaft Technologie. *89*, 504–520.

DEMAN, J.M. and FINORO, M. 1980. Characteristics of milk fat fractionated by crystallization from the melt. Canadian Inst. Food Sci. Technol. J. *13*(4), 167–173.

DREW, D.A. and HIXSON, A.N. 1944. The solubility relationships of high molecular weight fatty acids and their esters in propane near the critical temperature. Amer. Inst. Chem. Eng. Trans. *40*, 675–694.

EWING, F. 1935. US Patent 2,288,441.

FJAERVOL, A. 1970. The fractionation of milk fat, pp. 502–506, Dairy Industries.

FOUAD, F.M., VEN DE VOORT, F.R., MARSHALL, W.D. and FARRELL, P.G. 1990. Critical evaluation of thermal fractionation of butteroil. J. Amer. Oil Chem. Soc. *67*(12), 981–988.

HAMMAM, H., SODERBERG, I. and SIVIK, B. 1991. Physical properties of butter oil fractions obtained by supercritical carbon dioxide extraction. Food Sci. Technol. *93*, 374–378.

HIXSON, A.W. and HIXSON, A.N. 1941. The extraction of fatty acids from rosin acid-fatty acid mixtures by means of liquid propane. Amer. Inst. Chem. Eng. Trans. *37*, 927–954.

IVERSON, J.L. and SHEPPARD, A.J. 1986. Determination of fatty acids in butterfat using temperature programmed gas chromatography of butyl esters. Food Chem. *21*(3), 223–234.

JEBSON, R.S. 1970. Fractionation of milk fat into high and low melting point components. p. 240, XVIIIth International Dairy Congress.

JEBSON, R.S. 1974. Further studies in the fractionation of milk fat. p. 751, XIXth International Dairy Congress.

KANKARE, V. ANTILA, V., HARVALA, T. and KOMPPA, V. 1989. Extraction of milk fat with supercritical carbon dioxide. Milchwissenschaft. *44*, 407–411.

KURNIK, R.T., HOLLA, S.J. and REID, R.C. 1981. Solubility of solids in supercritical carbon dioxide and ethylene. J. Chem. Eng. Data. *26*, 47.

LUND, P. 1971. Analysis of butterfat triglycerides by capillary gas chromatography. Milchwissenschaft. *43*, 159–161.

✓ MATTIKOW, M. 1950. Refining fatty oils with liquid propane. J. Amer. Oil Chem. Soc. *27*, 11–14.

McHUGH, M. and KRUKONIS, V. 1986. Supercritical Fluid Extraction, Butterworths, Boston.

NAJOUR, G.C. and KING, A.D, Jr. 1966. Solubility of naphthalene in compressed methane, ethylene and carbon dioxide: evidence for a gas-phase complex between naphthalene and carbon dioxide. J. Chem. Physics. *45*, 1915.

NORRIS, G.E., GRAY, I.K. and DOLBY, R.M. 1973. Seasonal variations in the composition and thermal properties of New Zealand milk fat. J. Dairy Research. *40*, 311–321.

PASSINO, H.J. 1949. The Solexol process. Ind. Eng. Chem. *41*, 280–287.

RIZVI, S.S.H., DANIELS, J.A., BENADO, A.L. and ZOLLWEG, J.A. 1986. Supercritical fluid extraction: operating principles and food applications. Food Technol. *40*, 57–64.

RIZVI, S.S.H., LIM, S., NIKOOPOUR, M. and YU, Z. 1989. Supercritical fluid processing of milk fat. In *Engineering and Food*, Vol. 3, Elsevier Applied Science, New York.

SCHAAP, J.E., BADINGS, H.T., SCHMIDT, D.G. and FREDE, E. 1975. Differences in butterfat crystals, crystallized from acetone and the melt. Neth. Milk Dairy J. *29*, 242–252.

SHISHIKURA, A., FUJIMOTO, K., KANEDA, T. ARIA, K. and SAITO, S. 1986. Modification of butteroil by extraction with supercritical carbon dioxide. Agric. Biol. Chem. *50*, 1209–1215.

STRAVER, E.J.M., ROO, J.L. de, PETER, C.J. and SWAAN ARONS, J. de. 1991. Phase behavior of mixtures of near-critical propane with pure triglycerides and edible oils and fats. pp. 482–484. Proceedings 2nd Internat. Symp. on Supercritical Fluids, Boston, MA.

STRAVER, E.J.M., ROO, J.L. de, PETER, C.J. and SWAAN ARONS, J. de. 1993. Three phase behavior in binary mixtures of near-critical propane and triglycerides. Supercritical Fluid Engineering Science. Amer. Chem. Soc. Symp. Series. Washington, D.C.

TSEKHANSKAYA, Y.V., IOMTEV, M.B. and MUSHKINA, E.V. 1964. Solubility of naphthalene in ethylene and carbon dioxide under pressure. Russian J. Physical Chem. (English translation). *36*, 1177.

WILSON, R.E., KEITH, P.C., JR. and HAYLETT, R.E. 1936. The use of liquid propane in dewaxing, deasphalting and refining heavy oils. Amer. Inst. Chem. Eng. Trans. *32*, 364–406.

✓ YOON, J., HARTEL, R.W. and WANG, Y-C. 1993. Analysis of butterfat extraction and fractionation using supercritical carbon dioxide. J. Food Processing and Preservation *17*(6), 471–484.

OPTIMIZING A LACTIC FERMENTATION OF SLICED CARROTS

REGINA M. NABAIS[1] and F. XAVIER MALCATA[2]

Escola Superior de Biotecnologia
Universidade Catolica Portuguesa
Rua Dr. Antonio Bernardino de Almeida
4200 Porto, Portugal

Accepted for Publication August 2, 1995

ABSTRACT

Response surface methods were utilized in the statistical optimization of several quality factors pertaining to the preservation of carrot slices using a brine containing lactic acid produced by in situ fermentation. These factors were the concentrations of salt, acid, and reducing sugars, and the texture of the carrot material, and the pH, concentrations of acid, reducing sugars, and biomass (at two different times) of the brine. The processing variables considered were the temperature, the salt concentration of the brine, and the ratio of volumes of brine to the carrot material. The starting (corner and center) factorial design has indicated that, within the experimental range of practical interest, a linear model failed to provide a good fit to the experimental data; hence, this design was complemented with an axial design. Checks of the residuals and estimates of third-order parameters have indicated that no apparent reason existed to question the statistical adequacy of the quadratic empiric model. The loci of the optima (and the characterization of such optima) were then obtained for this model, and the general directions for the variation of the values of the processing parameters were presented. This study has indicated that temperature may be manipulated to give rise to any desired increase or decrease of the quality factor chosen, a conclusion that may be relevant in attempts to industrially improve carrot preservation processes based on lactic acid fermentation.

---

[1] Current address: Escola Superior Agraria de Coimbra, S. Martinho do Bispo, 3000 Coimbra, Portugal.

[2] To whom all correspondence should be addressed.

Journal of Food Processing and Preservation **19**(1995) 427–449. *All Rights Reserved*

INTRODUCTION

The preservation of such vegetables as carrots in low pH brines has been employed extensively using mainly one of two alternative routes: addition of food grade organic acids to the brines or in situ acidification by fermentation. The latter route possesses the particular advantage that the major factor responsible for the extension of the shelf life of the carrots, i.e., the low pH brought about by the presence of organic acids, is obtained at the expense of the metabolic use by the microorganisms of the sugars contributed to the solution by the carrots themselves, thus reducing undesirable secondary fermentations (Nicketic-Aleksic 1973; Fleming *et al.* 1983).

Lactic acid is an important tool in food grade fermentations because *Lactobacillus plantarum* (the most common strain employed), a facultative heterofermentative strain (Bergey 1989), possesses a very high acid tolerance (Fleming 1982), lactic acid is not toxic for human consumption (Adam and Hall 1988), and the low pH in the brines brought about by lactic acid prevents infections (Bell *et al.* 1972). Since the initial common pH of brines is ca. 5, most of the lactic acid remains in dissociated form ($pK_a = 3.86$), which is known to have a low inhibitory effect in desired microorganisms due to its slow rates of transport across their membrane (Adams and Hall 1988). The above reasoning, coupled with the observation that high acid concentrations in the medium strongly correlate with low pH values in the vegetable edible tissue (Moreira *et al.* 1988), make it of crucial importance to tailor a pickling fermentation process in order to achieve high rates of acid production immediately upon start up of the brining process (Adams and Hall 1988). Since lactic acid is a growthassociated product, such high rates of acid production are obtained at the expense of high growth rates of the lactic acid bacteria during, say, the first 24 to 48 h of brining.

Salt deliberately added to the brines plays an important role in pickling (Binsted *et al.* 1962). In fact, this solute helps leaching of water and reducing sugars from the vegetable tissues, and together with the organic acids helps inhibit the growth of undesirable microorganisms (Fleming 1982; Steinkraus 1983). However, excess of this solute has been implicated with such major changes in the vegetable structure as membrane shrinkage (Schwartzberg and Chao 1982), as well as the development of unwanted osmophilic microorganisms (Diez *et al.* 1985) and the inhibition of lactic acid production (Diez 1985). The current trend is towards the reduction of the overall inventory of salt in brining processes due to its pollution potential and to adverse health effects upon ingestion by consumers (Diez *et al.* 1985).

In addition to the detrimental effect of salt upon the vegetable cell membranes, softening enzymes initially present in the plant tissue or attack by microbial enzymes also cause loss of texture of fermented pickles (Fleming *et* *al.* 1983). Hence, it is a good practice in the manufacture of fermented pickles to generate as high a concentration of acid as possible not only because of its inhibitory effect on undesirable microorganisms during the primary fermentation but also because of the increase in the extent of sugar leaching with concomitant effects in the prevention of growth of spore-forming, spoilage bacteria and secondary fermentation yeasts on the fermentable sugars remaining in the carrot material (Fleming *et al.* 1983; Diez *et al.* 1985; Adam *et al.* 1988). However, low pH values also cause calcium shifts in the pectic substances (Diez *et al.* 1985), which may directly lead to extensive losses of texture, and so a compromise must be reached in order to obtain final pickles with good quality.

The transport of sugars from the carrot cells to the brine has been studied previously for relatively low temperatures by a number of authors (Steinkraus 1983; Potts *et al.* 1986; Nabais *et al.* 1995; Nabais and Malcata 1995), as well as the transport of lactic acid (Potts *et al.* 1986; Nabais *et al.* 1995; Nabais and Malcata 1995), and sodium chloride from the brine to the carrots (Nabais *et al.* 1995; Nabais and Malcata 1995). The fermentation of the sugars upon leaching from the vegetables to the brines by deliberately added microbial inocula has received the attention of several researchers (Nicketic-Aleksic 1973; Etchells 1973; Fleming 1982; Diez *et al.* 1985; Andersson *et al.* 1990). However, the conditions which lead to optimal values of predefined quality factors of the carrots has not been established to date in a simultaneously comprehensive and statistically sound manner.

It is the aim of this communication to report optimization efforts using response surface methodology for nine different quality factors using as predictive variables three processing factors which are easily manipulated.

EXPERIMENTAL METHODS

Previous experience has indicated that the temperature, the concentration of salt in the brine, and the ratio of the volumes of the brine and that of the carrots were three operating variables which should deserve careful study not only because their values can be easily manipulated, but also because they affect the properties of the final pickled carrots in a significant fashion. However, it should be borne in mind that practical limits exist for the ranges of variation of such processing variables because of organoleptic constraints posed by the final consummer.

In terms of quality factors, the choice is obviously much wider, and can be either associated with the properties of the brine or the properties of the carrots after a reasonable batch time has elapsed. Four quality factors associated with the carrots were considered in this analysis: (1) the concentration of chloride

TABLE 1.
STARTING (FIRST ORDER) EXPERIMENTAL DESIGN FOR TEMPERATURE (T), SALT CONCENTRATION IN THE BRINE (C), AND VOLUME VOLUME OF THE BRINE (V); EXPERIMENTAL DATA OBTAINED FOR THE CONCENTRATION OF CHLORIDE SALTS IN THE CARROT (S, %W/W), CONCENTRATION OF ACIDS IN THE CARROT (A, %W/W), CONCENTRATION OF REDUCING SUGARS IN THE CARROT (R, %W/W), TEXTURE OF THE CARROT (N, G_F/CM^2), PH OF THE BRINE (p), CONCENTRATION OF ACIDS IN THE BRINE (a, %W/V), CONCENTRATON OF REDUCING SUGARS IN THE BRINE (r, %W/V), CONCENTRATION OF BIOMASS AFTER 24 H IN THE BRINE (f, %W/V), AND FINAL CONCENTRATION OF BIOMASS IN THE BRINE (x, %W/V); VALUES OF MAIN EFFECTS; CHECS OF SECOND ORDER INTERACTIONS (12, 13, AND 23); AND CHECKS OF QUADRATIC CURVATURE (11+22+33). (RUNS WERE MADE IN RANDOM ORDER.)

		E				LoF				MV CM				MVB				
	U	(I)	(1)	(2)	(3)	(12)	(13)	(23)	(11)+(22)+(33)	S	A	R	N	p	a	r	f	x
C	1	+1	-1	-1	-1					0.42	0.87	0.51	0.95	3.20	1.04	1.56	0.31	1.36
	2	+1	-1	-1	+1					0.82	0.50	0.19	0.75	3.50	0.67	0.39	0.27	0.65
	3	+1	-1	+1	-1					2.87	0.45	0.65	0.94	3.50	0.52	3.04	0.26	0.98
	4	+1	-1	+1	+1					3.80	0.18	0.42	0.87	4.40	0.35	2.43	0.24	0.60
	5	+1	+1	-1	-1					0.51	0.69	0.74	0.90	3.30	0.70	4.46	0.53	0.62
	6	+1	+1	-1	+1					0.99	0.30	0.31	0.61	3.90	0.40	1.92	0.36	0.48
	7	+1	+1	+1	-1					3.50	0.22	0.73	0.98	3.50	0.39	5.89	0.36	0.67
	8	+1	+1	+1	+1					4.37	0.09	0.49	0.65	4.60	0.12	6.50	0.25	0.39
c	9	+1	0	0	0					2.33	0.41	0.33	0.86	3.60	0.35	1.05	0.41	0.56
	10	+1	0	0	0					2.31	0.43	0.34	1.08	3.65	0.39	1.00	0.41	0.54
	11	+1	0	0	0					2.33	0.43	0.31	1.10	3.60	0.39	0.95	0.40	0.57
EE ±t.σ	S	2.2045 ±0.0077	-0.1825 ±0.0094	1.4750 ±0.0094	0.3350 ±0.0094	0.1175 ±0.0094	0.0025 ±0.0094	0.1150 ±0.0094	-0.1633 ±0.0177									
	A	0.4155 ±0.0077	-0.0875 ±0.0094	-0.1775 ±0.0094	-0.1450 ±0.0094	0.0075 ±0.0094	0.0150 ±0.0094	0.04500 ±0.0094	-0.0108 ±0.0177									
	R	0.4564 ±0.0101	0.0625 ±0.0125	0.0675 ±0.0125	-0.1525 ±0.0125	-0.0250 ±0.0125	-0.0150 ±0.0125	0.0350 ±0.0125	0.1783 ±0.0234									
	N	0.8809 ±0.0884	-0.0463 ±0.1086	0.0288 ±0.1086	-0.1113 ±0.1086	0.0013 ±0.1086	-0.0438 ±0.1086	0.0113 ±0.1086	-0.1821 ±0.1639									
	p	3.7045 ±0.0192	0.0875 ±0.0235	0.2625 ±0.0235	0.3625 ±0.0235	-0.0375 ±0.0235	0.0625 ±0.0235	0.1375 ±0.0235	0.1208 ±0.0442									
	a	0.4836 ±0.0153	-0.1213 ±0.0188	-0.1788 ±0.0188	-0.1388 ±0.0188	0.0313 ±0.0188	-0.0038 ±0.0188	0.0288 ±0.0188	0.1471 ±0.0354									
	r	2.6536 ±0.0332	1.4188 ±0.0408	1.1913 ±0.0408	-0.4638 ±0.0408	0.3113 ±0.0408	-0.0188 ±0.0408	0.4638 ±0.0408	2.2738 ±0.0766									
	f	0.3455 ±0.0038	0.0525 ±0.0047	-0.0450 ±0.0047	-0.0425 ±0.0047	-0.0250 ±0.0047	-0.0275 ±0.0047	0.0100 ±0.0047	-0.0842 ±0.0088									
	x	0.6745 ±0.0101	-0.1788 ±0.0125	-0.0588 ±0.0125	-0.1888 ±0.0125	0.0488 ±0.0125	0.0838 ±0.0125	0.0238 ±0.0125	0.1621 ±0.0234									

Note: c - Center points; C - Corner points; EE - Estimated Effects; E - Effects (linear); I - grand average; LoF - Lack of Fit analysis; MV CM - Measured Values for the Carrot Material; MV B - Measured Values for the Brine; *t* - probability point of Student's *t*-distribution; U - run; 1 - Normalized value of temperature, defined as (T-30)/10, where T is expressed in °C; 2 - Normalized concentration of salt in the brine, defined as (C-4)/3, where C is expressed in g/L; 3 - Normalized volume of brine, defined as (V-375)/275, where V is expressed in mL; and σ - standard deviation.

salt(s), (2) the concentration of acid(s), (3) the concentration of reducing sugars, and (4) the texture. Five quality factors associated with the brine were also considered: (1) the pH, (2) the concentration of acid(s), (3) the concentration of reducing sugars, (4) the concentration of biomass after 24 h, and (5) the concentration of biomass at the end of the batch. The experimental results for all eight properties obtained according to the starting design are tabulated in Table 1, whereas the results obtained following the composite design are listed in Table 2.

Materials

Fresh carrots were bought at random at local markets (dominating cultivar: Nantes). Sodium chloride, sodium hydroxide, potassium dichromate, copper sulphate, potassium permanganate, and silver nitrate were purchased from Merck (Frankfurt, Germany). Dinitrosalicilic acid was obtained from BDH Laboratory Supplies (Dorset, England). The inocula of *Lactobacillus plantarum* (LP no. 91249 G-2) were a gift from Textel/Lactolabo from Marshall (Madrid, Spain). MRS broth and YNB were purchased from Oxoid (Hampshire, UK). Yeast Extract was obtained from Difco (Detroit, USA) and anhydrous D(+)-glucose from Merck (Frankfurt, Germany).

Equipment

Centrifugations were performed in a Universal Hettich Centrifuge (Tuttlingen, Germany). Titrations were done with a titroprocessor model 682 connected to a Dosimat Model 665 equipped with the combined glass electrode 60202100, all from Metrohm (Herisau, Switzerland). Measurements of pH were done with a titrator from Crisson (Barcelona, Spain) equipped with the combined electrode 104023311 from Ingold (Steinbach, Switzerland). Isothermal conditions and stirring were achieved using thermostatted shaker baths Kotterman 3047 from Labortechnik (Amtsmtsgerich Burgdorf, Germany). Spectrophotometric measurements were made with a Spectrophotometer Model 350 from Pye Unicam (Cambridge, UK). Sterilization was achieved in a laboratory retort Austester Model 437G from Selecta (Barcelona, Spain). A scale Model PC 2000 from Mettler (Greifensee, Switzerland) was used for rough weight determinations, whereas accurate weight determinations were done with an analytical balance Model S 2000 from Bosch (Jungingen, Germany). A sensor thermometer Model G90200 from Cole Parmer (Niles, Illinois, USA) was employed to measure the temperature of the solutions before calibration of the titroprocessor. Isothermal chambers Model B80 from Memmert (Schwabach, Germany) and

Model 750E from Fitoclima (Lisboa, Portugal) were used for drying and incubating, respectively. The texture of the carrots (hardness) was evaluated with a texture analyser from Stevens LFRA (Essex, UK) using the probe TA9.

Methods

Preparation of the Inocula. Following opening of the package, the inoculum microorganisms were mainted at 7C and weekly reseeded in Petri dishes on MRS agar. From these dishes, a portion was removed and incubated for 12 h in MRS medium (50 ml) at 30C, and then for an extra 12 hr at room temperature. Following this period, the suspension of cells was sequentially centrifugated and washed with 0.85%(w/v) of sodium chloride. The cell precipitate was resuspended in sterilized deionized water in a volume sufficient to obtain the desired concentration of inoculum, which was then used for actual fermentation batches in the ratio of 1 ml of inoculum per 100 ml of solution; the concentration corresponded to an optical density at 640 nm (OD_{640}) of ca. 0.100.

Performance of Experimental Fermentations. Brines were prepared at 25C using the appropriate amounts of sodium chloride (previously dried overnight to constant weight) in deionized water. The brines were sterilized for 15 min in a laboratory retort.

Before starting each experiment, the carrots had both tops cut off, and were thoroughly washed with tap water, submerged for 1.5 min in a 0.2% (w/v) copper sulphate solution, submerged for 2 min in a 0.2% (w/v) potassium permanganate solution, and finally rinsed with an aqueous solution of the same salt concentration to be used in that experiment. Carrots were then sliced into 1-cm high pieces, and 12 pieces of the disinfected carrots were submerged in the aforementioned brines. Soon after thermal equilibrium was reached, the brines were inoculated with 1 ml of inoculum, and gently stirred in an uniform fashion using a shaker bath (orbital setting speed: 5).

Analysis of Sodium Chloride. After removal from the brines, the carrot slices were quickly rinsed with deionized water, slightly dried with tissue paper, cut into very small pieces, submerged in 50 ml of deionized water in a stoppered flask, and heated for 30 min in a laboratory retort according to the method by McKnee (1985). Upon cooking, the carrot pieces together with the aqueous extract were homogenized and centrifuged for 10 min at 5,000 rpm. Finally, 2 ml of the clarified supernatant liquid were titrated with a standard solution of 0.05 N silver nitrate using potassium dichromate as indicator.

Analysis of Lactic Acid. The lactic acid was measured via determination of the total acidity of the solution expressed as lactic acid equivalent. An aliquot of 2 ml of the clarified extract (obtained as described in the previous subsection) was diluted in 50 ml of deionized water, titrated with 0.01 N solution of sodium hydroxide until a final pH of 8.2 is reached and maintained for 99 s using an automatic titrator; the titre of the blank was deducted accordingly.

Analysis of pH. The pH of the brine was determined using an automatic pH meter with a combined glass electrode.

Analysis of Reducing Sugars. Aliquots of the brines were periodically taken, diluted with deionized water, and analyzed following the dinitrosalicilic acid method of Miller (1959). The results were expressed as glucose equivalent. The concentration of reducing sugars remaining in the carrot material was determined by analyzing, using the same method, the clarified extract (obtained as described in the subsection *Analysis of sodium chloride*).

Analysis of Texture. The texture of the carrots, defined for our purposes as the hardness of the carrots, was evaluated with the texture analyser.

Analysis of Biomass. The concentration of cells (in g/L) was estimated from a calibration curve. The resuspended inoculum at the adequate dilution was used in the proportion of 1 ml per 100 ml of sterilized broth of YNB added with 10 g of glucose per L and 2.5 g of yeast extract per L so that the initial optical density of the culture medium at 640 nm (OD_{640}) was ca. 0.100 (deionized water used as blank). The growth of the microorganisms was followed by reading the optical density at the same wavelength in the range 0.1–0.5. The samples obtained at each reading were subject to multiple centrifugation and washing steps, and the biomass dried at 60C until a constant final weight (ca. 48 h). A fit of a linear model yielded the equation $BM(g/L)=0.289\ OD_{640}+0.0605$, where BM is the biomass concentration expressed as dry cell weight (correlation coefficient of 0.95).

STATISTICAL METHODS

The experiments were designed in a sequential fashion starting with an eight-point, full, two-way factorial design coupled with three center points (i.e., three replicates used as estimators of variance) (Box *et al.* 1978) aiming at fitting the following four-parameter linear model:

$$\hat{y}_{i,j} = b_{0;j} + b_{1;j}\, x_{1,j} + b_{2;j}\, x_{2,j} + b_{3;j}\, x_{3,j} \qquad (1)$$

Here $\hat{y}_{i,j}$ is the estimated value for the *j*-th quality factor (i=1,2,...,8) in the *i*-th experiment (j=1,2,...,11), the $b_{i;j}$'s (i=0,1,2,3) are parameters associated with the *j*-th quality factor to be fitted by linear regression analysis, and the x_{ij}'s (i=1,2,3) are the predictors associated with the *j*-th quality factor and the *i*-th experiment. The results obtained for the parameters are tabulated in Table 1 together with their 95% marginal confidence intervals (the formulas utilized are listed as Appendix). Diagnostic checks were performed on the values of each of the three two-way interaction effects and on the magnitude of the sum of the three quadratic effects. The values of these diagnostics are also tabulated in Table 1.

The results of the measurements for all quality factors tested obtained from the data set generated according to the starting design have indicated that the linear model was inappropriate; hence, a further set of eight experiments was performed in order to form a composite design with nineteen experimental points. The eight new experiments were performed as three sets of two experiments laid out as star points (as opposed to the corner points used in the previous design) coupled with two extra center points (which were combined with the previous three replicates in the calculation of a new improved estimate of variance with fewer degrees of freedom) (Box *et al.* 1978). In this case, the following ten-parameter quadratic model was entertained:

$$\hat{y}_{i,k} = b_{0;k} + b_{1;k}\,x_{1,k} + b_{2;k}\,x_{2,k} + b_{3;k}\,x_{3,k} + b_{11;k}\,x_{1,k}^{2} + b_{22;k}\,x_{2,k}^{2} + \ldots \qquad (2)$$
$$\ldots\; b_{33;k}\,x_{3,k}^{2} + b_{12;k}\,x_{1,k}\,x_{2,k} + b_{13;k}\,x_{1,k}\,x_{3,k} + b_{23;k}\,x_{2,k}\,x_{3,k}$$

where the $b_{j;k}$'s (j=0,1,2,3; k=1,2,...,8) are linear parameters and the $b_{jl;k}$'s (j=1,2,3; l=1,2,3; k=1,2,...,8) are quadratic (or second order) parameters to be fitted by linear regression analysis. The results obtained for the parameters using the full composite design are tabulated in Table 2 together with their 95% marginal confidence intervals (the formulas utilized are listed as Appendix). Diagnostic checks were performed in order to assess the validity of the quadratic model in view of the possibility of employing a cubic model. The value of the three-way interaction effect and the magnitude of the cubic effects along each of the three spatial directions (corresponding to the three predictors x_1, x_2, and x_3) are tabulated in Table 2. The magnitude of the block effect between the first and the second part of the design is also included in this table.

Since statistical considerations have indicated that no need exists for a cubic model, the best estimates of the parameters in Eq.(2) were further utilized to find the analytical expressions for the loci of the critical points and to decide on the nature of such points. The results of this analysis are depicted in Table 3 (the formulas utilized are listed as Appendix).

DISCUSSION AND CONCLUSIONS

In the designing of the experiments, a sequential methodology was followed. This means that a block of eleven experiments was performed initially. Since the data generated by the initial design revealed general inadequacy of the linear model, the design was complemented with another block of eight experiments at a later stage. The possible existence of block to block differences was checked via comparison of the average of the three center points of the starting design with the average of the two center points of the secondary design (see column block in Table 2), which, in all cases, has shown to be statistically not significant. The general adequacy of the assumptions underlying the validity of the regression analyses pertaining to the quadratic model (i.e., normal distribution of residuals and constant variance) was double checked via diagnostics of the residuals (see Fig.1) which did not reveal significant bias.

The major goal of the above analysis was to determine the equations of the lines which contain all maxima (or all minima, depending on the type of optima as depicted in Table 3) for every predictor given the values for the other two predictors. Such equations give at once the best value for the predictor in question if the other two are set by any other processing or heuristic constraint. Inspection of Table 3 indicates that a true maximum for all three predictors considered together exists only for the salt concentration in the carrot, although the location of such overall maximum is beyond physical realizability; remember that, given the definition of variables x_1, x_2, and x_3 as linear functions of **T**, **C**, and **V**, respectively, practical constraints read $-3 < x_1 < +7$, $-4/3 < x_2 < +10$, and $-15/11 < x_3$. For all quality factors but **S**, no overall local optimum exists, which mathematically is equivalent to say that the coordinates in the **MM** column define saddle points (Box *et al.* 1978); in these cases, the maximum (or the minimum) values of the optima lie on physical constraints.

The objectives underlying the improvement of the processing conditions of the manufacture of carrot pickles are to increase the values of **A**, **N**, **a**, **x**, and **f**, and to decrease the values of **S**, **R**, **p**, and **r**. From inspection of Table 3, it is clear that only x_1 should be manipulated to obtain the desired optimum in the case of **A** and **a**, either x_1 or x_2 in the cases of **R**, **p**, **r**, **f**, and **x**, and only x_2 in the case of **N**. The directions of manipulation are given by the analytical expressions of the optima tabulated in the **LO** column of Table 3.

It is interesting to note that temperature is ubiquitous in the optimization procedures except for the texture, which makes it a particularly suitable variable for manipulation in view of the preset objective functions. Therefore, within the limits of practical interest for the processing variable in question (and assuming that both x_2 and x_3 do not violate the constraints set forth before), factors **S**, **A**, **a**, **f**, and **x** pass through true local maxima and factors **R**, **p**, and **r** pass through

TABLE 2.

COMPOSITE (SECOND ORDER) EXPERIMENTAL DESIGN FOR TEMPERATURE (T), SALT CONCENTRATION IN THE BRINE (C), AND VOLUME OF THE BRINE (V); EXPERIMENTAL DATA OBTAINED FOR THE CONCENTRATION OF CHLORIDE SALTS IN THE CARROT (S, %W/W), CONCENTRATION OF ACIDS IN THE CARROT (A, %W/W), CONCENTRATION OF REDUCING SUGARS IN THE CARROT (R, %w/w), TEXTURE OF THE CARROT (N, G_F/CM^2), PH OF THE BRINE (p), CONCENTRATION OF ACIDS IN THE BRINE (a, %W/V), CONCENTRATON OF REDUCING SUGARS IN THE BRINE (r, %W/V),CONCENTRATION OF BIOMASS AFTER 24 H IN THE BRINE (f, %W/V), AND FINAL CONCENTRATION OF BIOMASS IN THE BRINE (x, %W/V); VALUES OF MAIN LINEAR EFFECTS (1, 2, AND 3); VALUES OF MAIN QUADRATIC EFFECTS (11, 22, AND 33); VALUES OF SECOND-ORDER INTERACTIONS (12, 13, AND 23); CHECKS OF THIRD-ORDER INTERACTIONS (123); CHECKS OF CUBIC CURVATURE (111-122/3-133/3, 222-112/3-233/3, AND 333-113/3-223/3); AND CHECKS OF BLOCK EFFECTS. (RUNS WERE MADE IN RANDOM ORDER.)

		E&I									
	U	(I)	(1)	(2)	(3)	(11)	(22)	(33)	(12)	(13)	(23)
C	1	+1	-1	-1	-1	+1	+1	+1	+1	+1	+1
	2	+1	-1	-1	+1	+1	+1	+1	+1	-1	-1
	3	+1	-1	+1	-1	+1	+1	+1	-1	+1	-1
	4	+1	-1	+1	+1	+1	+1	+1	-1	-1	+1
	5	+1	+1	-1	-1	+1	+1	+1	-1	-1	+1
	6	+1	+1	-1	+1	+1	+1	+1	-1	+1	-1
	7	+1	+1	+1	-1	+1	+1	+1	+1	-1	-1
	8	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1
c	9	+1	0	0	0	0	0	0	0	0	0
	10	+1	0	0	0	0	0	0	0	0	0
	11	+1	0	0	0	0	0	0	0	0	0
c	12	+1	0	0	0	0	0	0	0	0	0
	13	+1	0	0	0	0	0	0	0	0	0
ax	14	+1	-1	0	0	+1	0	0	0	0	0
	15	+1	+1	0	0	+1	0	0	0	0	0
	16	+1	0	-1	0	0	+1	0	0	0	0
	17	+1	0	+1	0	0	+1	0	0	0	0
	18	+1	0	0	-1	0	0	+1	0	0	0
	19	+1	0	0	+1	0	0	+1	0	0	0
EE ±t.σ	S	2.4449±0.0478	0.2200±0.0702	1.504±0.0702	0.349±0.0702	-0.0411±0.0702	-0.0511±0.0702	-0.1761±0.0702	0.1175±0.0812	0.0025±0.0812	0.115±0.0812
	A	0.3482±0.0292	-0.0900±0.0429	-0.1980±0.0429	-0.1540±0.0429	-0.1286±0.0429	0.0714±0.0429	0.1114±0.0429	0.0075±0.0496	0.0150±0.0496	0.0450±0.0496
	R	0.2702±0.0395	0.0650±0.0580	0.0830±0.0580	-0.1390±0.0580	0.2395±0.0580	0.0295±0.0580	-0.0505±0.0580	-0.0250±0.0671	-0.0150±0.0671	0.0350±0.0671
	T	0.9438±0.0564	-0.0310±0.0828	0.0610±0.0828	-0.0940±0.0828	0.0489±0.0828	-0.1711±0.0828	0.0039±0.0828	0.0013±0.0958	-0.0438±0.0958	0.0113±0.0958
	p	3.3077±0.1476	0.1600±0.2166	0.3400±0.2166	0.2800±0.2166	0.3201±0.2166	0.3201±0.2166	-0.2799±0.2166	-0.0375±0.2506	0.0625±0.2506	0.1375±0.2506
	a	0.3696±0.0299	-0.1130±0.0439	-0.2060±0.0439	-0.1570±0.0439	-0.1441±0.0439	0.1509±0.0439	0.1359±0.0439	0.0313±0.0508	-0.0038±0.0508	0.0288±0.0508
	r	1.5911±0.4041	1.7200±0.5929	1.3750±0.5929	-0.3500±0.5929	1.3049±0.5929	0.4899±0.5929	-0.0450±0.5929	0.3113±0.6861	-0.0188±0.6861	0.4638±0.6861
	f	0.3508±0.0232	0.0350±0.0340	-0.0550±0.0340	-0.0600±0.0340	-0.0969±0.0340	-0.0069±0.0340	0.0681±0.0340	-0.0250±0.0394	-0.0275±0.0394	0.0100±0.0394
	x	0.6342±0.0527	-0.1580±0.0773	-0.0630±0.0773	-0.2140±0.0773	-0.0870±0.0773	-0.0020±0.0773	0.1730±0.0773	0.0488±0.0894	0.0838±0.0894	0.0238±0.0894

TABLE 2. (cont.)

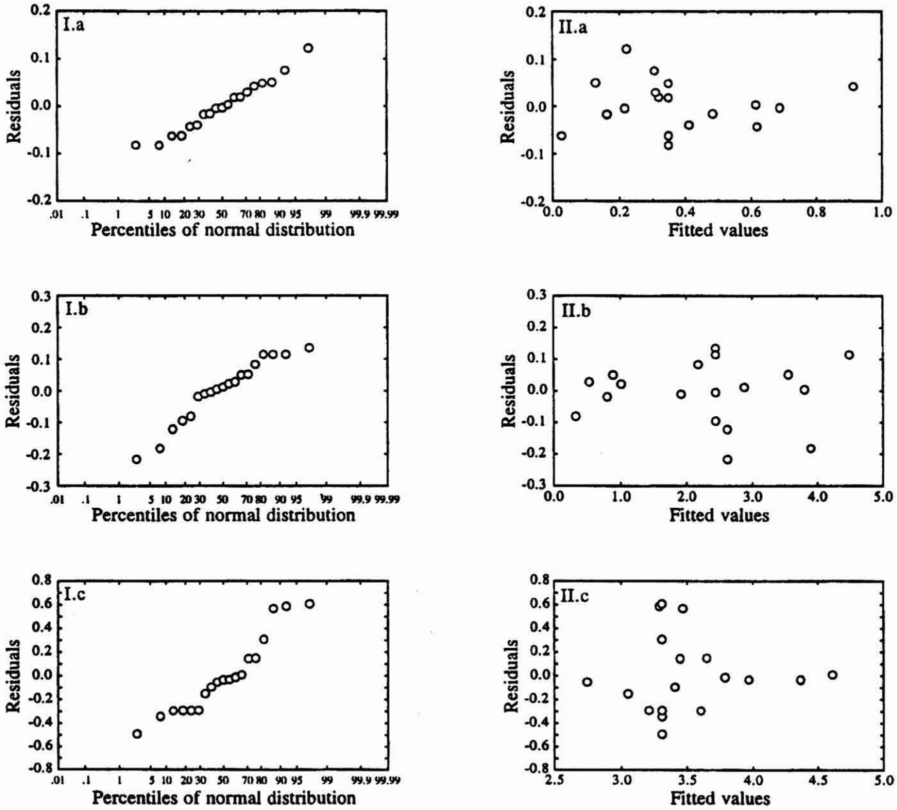
		LoF					MV CM				MV B				
	U	(123)	(111)	(222)	(333)	block	S	A	R	T	p	a	r	f	x
C	1						0.42	0.87	0.51	0.95	3.20	1.04	1.56	0.31	1.36
	2						0.82	0.50	0.19	0.75	3.50	0.67	0.39	0.27	0.65
	3						2.87	0.45	0.65	0.94	3.50	0.52	3.04	0.26	0.98
	4						3.80	0.18	0.42	0.87	4.40	0.35	2.43	0.24	0.60
	5						0.51	0.69	0.74	0.90	3.30	0.70	4.46	0.53	0.62
	6						0.99	0.30	0.31	0.61	3.90	0.40	1.92	0.36	0.48
	7						3.50	0.22	0.73	0.98	3.50	0.39	5.89	0.36	0.67
	8						4.37	0.09	0.49	0.65	4.60	0.12	6.50	0.25	0.39
c	9						2.33	0.41	0.33	0.86	3.60	0.35	1.05	0.41	0.56
	10						2.31	0.43	0.34	1.08	3.65	0.39	1.00	0.41	0.54
	11						2.33	0.43	0.31	1.01	3.60	0.49	0.95	0.40	0.57
c	12						2.45	0.33	0.20	0.88	3.80	0.35	1.00	0.30	0.77
	13						2.54	0.30	0.43	0.89	3.00	0.45	2.88	0.35	0.74
ax	14						2.10	0.28	0.37	0.94	2.90	0.26	0.24	0.26	0.62
	15						2.84	0.08	0.52	1.00	3.80	0.10	6.09	0.19	0.47
	16						0.84	0.66	0.09	0.56	2.70	0.79	0.24	0.41	0.71
	17						4.08	0.10	0.38	0.94	4.00	0.16	4.46	0.22	0.55
	18						1.93	0.61	0.24	0.95	2.80	0.69	1.71	0.52	1.12
	19						2.74	0.23	0.07	0.90	2.70	0.23	1.92	0.26	0.49
EE ±t.σ	S	-0.0175±0.0812	0.1875±0.1816	0.1450±0.1816	0.0700±0.1816	0.1717±0.2893									
	A	0.0200±0.0496	-0.0125±0.1109	-0.1025±0.1109	-0.0450±0.1109	-0.1083±0.1767									
	R	0.0125±0.0671	0.0125±0.1500	0.0775±0.1500	0.0675±0.1500	-0.0117±0.2390									
	T	-0.0213±0.0958	0.0763±0.2143	0.1613±0.2143	0.0863±0.2143	-0.1283±0.3415									
	p	0.0125±0.2506	0.3625±0.5604	0.3875±0.5604	-0.4125±0.5604	-0.2167±0.8929									
	a	-0.0213±0.0508	0.0413±0.1136	-0.1363±0.1136	-0.0913±0.1136	-0.0100±0.1809									
	r	0.3238±0.6861	1.5063±1.5341	0.9188±1.5341	0.5688±1.5341	0.9400±2.4444									
	f	0.0050±0.0394	-0.0875±0.0880	-0.0500±0.0880	-0.0875±0.0880	-0.0817±0.1402									
	x	-0.0588±0.0894	0.1038±0.1999	-0.0213±0.1999	-0.1263±0.1999	0.1983±0.3186									

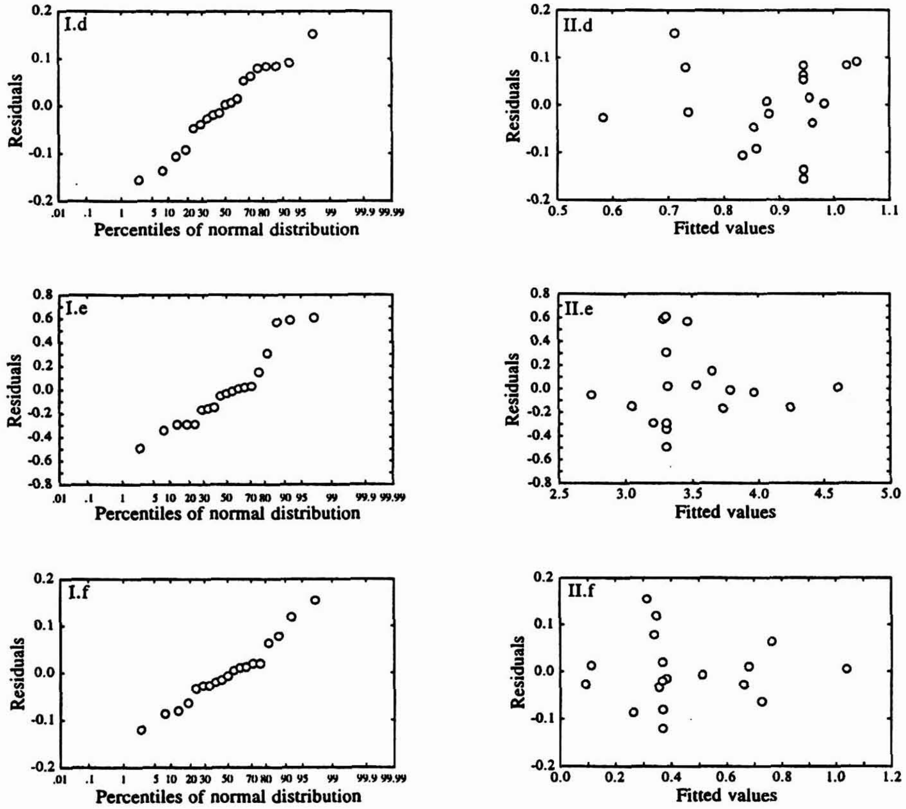
Note: ax - axial points; c - Center points; C - Corner points; EE - Estimated Effects; E&I - Effects (linear and quadratic) and Interactions (second order); I - grand average; LoF - Lack of Fit analysis; MV CM - Measured Values for the Carrot Material; MV B - Measured Values for the Brine;*t* - probability point of Student's *t*-distribution; U - rUn; 1 - Normalized value of temperature, defined as (T-30)/10, where T is expressed in C; 2 - Normalized concentration of salt in the brine, defined as (C-4)/3, where C is expressed in g/L; 3 - Normalized volume of brine, defined as (V-375)/275, where V is expressed in mL; and σ - standard deviation.

TABLE 3.
LOCI AND TYPE OF OPTIMA IN EACH OF THE OPERATING VARIABLES TEMPERATURE (x_1), SALT CONCENTRATION IN THE BRINE (x_2), AND VOLUME OF THE BRINE (x_3) ASSOCIATED WITH THE QUADRATIC MODELS FITTED TO THE DATA OBTAINED FOR THE CONCENTRATION OF CHLORIDE SALTS IN THE CARROT (S), CONCENTRATION OF ACIDS IN THE CARROT (A), CONCENTRATION OF REDUCING SUGARS IN THE CARROT (R), TEXTURE OF THE CARROT (N), PH OF THE BRINE (p), CONCENTRATION OF ACIDS IN THE BRINE (a), CONCENTRATON OF REDUCING SUGARS IN THE BRINE (r), AND CONCENTRATION OF BIOMASS IN THE BRINE (x).

		LO			TO			MM		
		x_1	x_2	x_3	x_1	x_2	x_3	x_1	x_2	x_3
EE	**S**	$2.6739 + 1.4281 x_2 + 0.0304 x_3$	$14.7065 + 1.1489 x_1 + 1.1245 x_3$	$0.9907 + 0.0071 x_1 + 0.3265 x_2$	max	max	max	-23.7278	-18.3771	-5.1771
	A	$- 0.3500 + 0.0292 x_2 + 0.0583 x_3$	$1.3857 - 0.0525 x_1 - 0.3149 x_3$	$0.6909 - 0.0673 x_1 - 0.2019 x_2$	max	min	min	-0.2867	1.2570	0.4564
	R	$- 0.1357 + 0.0522 x_2 + 0.0313 x_3$	$- 1.4051 + 0.4232 x_1 - 0.5925 x_3$	$- 1.3772 - 0.1486 x_1 + 0.3468 x_2$	min	min	max	-0.2143	-0.5796	-1.5464
	N	$0.3169 - 0.0128 x_2 + 0.4472 x_3$	$0.1783 + 0.0037 x_1 + 0.0329 x_3$	$11.9926 + 5.5817 x_1 - 1.4353 x_2$	min	max	min	-3.8590	-0.1430	-9.3421
	p	$- 0.2499 + 0.0586 x_2 - 0.0976 x_3$	$- 0.5311 + 0.0586 x_1 - 0.2148 x_3$	$0.5002 + 0.1117 x_1 + 0.2456 x_2$	min	min	max	-0.3166	-0.6169	0.3133
	a	$- 0.3921 + 0.1085 x_2 - 0.0130 x_3$	$0.6824 - 0.1035 x_1 - 0.0952 x_3$	$0.5775 + 0.0138 x_1 - 0.1058 x_2$	max	min	min	-0.3262	0.6684	0.5023
	r	$- 0.6590 - 0.1193 x_2 + 0.0072 x_3$	$- 1.4032 - 0.3176 x_1 - 0.4733 x_3$	$- 3.8849 - 0.2081 x_1 + 5.1475 x_2$	min	min	max	-0.7000	0.1713	-2.8572
	f	$0.1807 - 0.1291 x_2 - 0.1420 x_3$	$4.0113 - 1.8233 x_1 + 0.7293 x_3$	$0.4402 + 0.2018 x_1 - 0.0734 x_2$	max	max	min	0.6355	-4.5139	0.8997
	x	$- 0.9079 + 0.2801 x_2 + 0.4813 x_3$	$- 15.6687 + 12.1246 x_1 + 5.9068 x_3$	$0.6185 - 0.2421 x_1 - 0.0686 x_2$	max	max	min	3.5648	18.5768	-1.5196

Note: **EE** - Estimated Effects; **LO** - Loci of Optima; **MM** - Minimum of Maxima, Minimum of Minima, Maximum of Minima, or Maximum of Maxima; **TO** - Type of Optima.


I.a
Residuals
0.2
0.1
0.0
-0.1
-0.2
.01 .1 1 5 10 20 30 50 70 80 90 95 99 99.9 99.99
Percentiles of normal distribution
II.a
Residuals
0.2
0.1
0.0
-0.1
-0.2
0.0 0.2 0.4 0.6 0.8 1.0
Fitted values
I.b
Residuals
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
.01 .1 1 5 10 20 30 50 70 80 90 95 99 99.9 99.99
Percentiles of normal distribution
II.b
Residuals
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
0.0 1.0 2.0 3.0 4.0 5.0
Fitted values
I.c
Residuals
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
.01 .1 1 5 10 20 30 50 70 80 90 95 99 99.9 99.99
Percentiles of normal distribution
II.c
Residuals
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
2.5 3.0 3.5 4.0 4.5 5.0
Fitted values


I.d
Residuals
0.2
0.1
0.0
-0.1
-0.2
.01 .1 1 5 10 20 30 50 70 80 90 95 99 99.9 99.99
Percentiles of normal distribution
II.d
Residuals
0.2
0.1
0.0
-0.1
-0.2
0.5 0.6 0.7 0.8 0.9 1.0 1.1
Fitted values
I.e
Residuals
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
.01 .1 1 5 10 20 30 50 70 80 90 95 99 99.9 99.99
Percentiles of normal distribution
II.e
Residuals
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
2.5 3.0 3.5 4.0 4.5 5.0
Fitted values
I.f
Residuals
0.2
0.1
0.0
-0.1
-0.2
.01 .1 1 5 10 20 30 50 70 80 90 95 99 99.9 99.99
Percentiles of normal distribution
II.f
Residuals
0.2
0.1
0.0
-0.1
-0.2
0.0 0.2 0.4 0.6 0.8 1.0 1.2
Fitted values

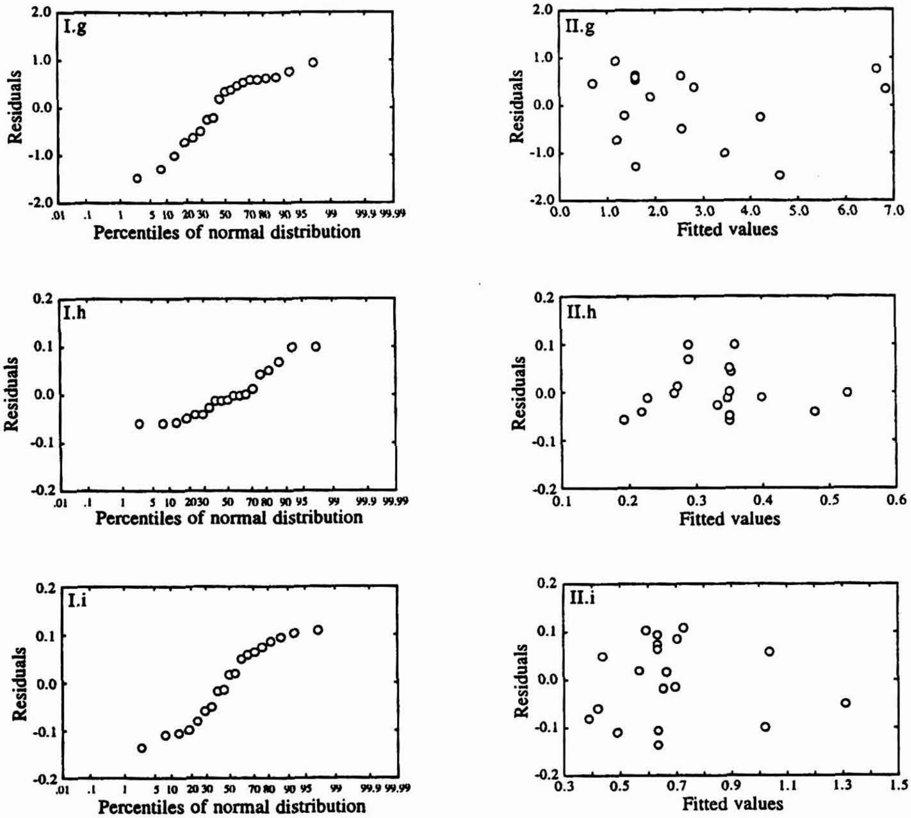


FIG. 1. PLOT OF RESIDUALS VERSUS (I) THE PERCENTILES OF A NORMAL DISTRIBUTION AND (II) THE FITTED VALUES, FOR DATA PERTAINING TO THE ACID CONTENT OF THE CARROTS (a), THE SALT CONTENT OF THE CARROTS (b), THE SUGAR CONTENT OF THE CARROTS (c), THE TEXTURE OF THE CARROTS (d), THE pH OF THE BRINE (e), THE CONCENTRATION OF ACID IN THE BRINE (f), THE CONCENTRATION OF REDUCING SUGARS IN THE BRINE (g), THE CONCENTRATION OF BIOMASS IN THE BRINE AFTER 24 H (h), AND THE CONCENTRATION OF BIOMASS IN THE BRINE AFTER COMPLETION OF THE BATCH (i)

local minima. It should be realized that for every combination of x_2 and x_3, a different value of the aforementioned optimum is obtained as given by the equations listed in the first row of Table 3; for the sake of information, it can be said that for factors **A** and **a** the worst of the optima, i.e. the minimum value for the maxima (as can be concluded from inspection of the last two rows of Table 3) is obtained when temperature takes the values 27.1 and 26.7C, respectively. By the same token, if the salt concentration is the processing variable elected for manipulation, texture passes through a true local maximum, and the worst of the optima thus obtained corresponds to having a brine 3.6 g/L in sodium chloride. The information generated in this research effort is useful in predesigning carrot preservation processes based on lactic fermentation.

NOMENCLATURE

a = concentration of acids in the brine (%w/v)
A = concentration of acids in the carrot (%w/w)
$b_{i,j}$ = parameter associated with the linear effect of x_i in the *j*-th quality factor
$b_{ii;j}$ = parameter associated with the quadratic effect of x_i in the *j*-th quality factor
$b_{ij;k}$ = parameter associated with the effect of the interaction of x_i and x_j in the *k*-th quality factor
C = salt concentration in the brine (g/L)
f = concentration of biomass after 24 h in the brine (%w/v)
N = texture of the carrot (g_f/cm^2)
p = pH of the brine
r = concentration of reducing sugars in the brine (%w/v)
R = concentration of reducing sugars in the carrot (%w/w)
T = temperature (C)
V = volume of the brine (ml)
S = concentration of chloride salts in the carrot (%w/w)
x = final concentration of biomass in the brine (%w/v)
x_1 = normalized value of temperature, (**T**-30)/10
x_2 = normalized concentration of salt in the brine, (**C**-4)/3
x_3 = normalized volume of brine, (**V**-375)/275
$y_{i,j}$ = estimated value for the *j*-th quality factor obtained in the *i*-th experiment
$\hat{y}_{i,j}$ = experimental value for the *j*-th quality factor obtained in the *i*-th experiment

FORMULAE UTILIZED TO GENERATE THE CANONICAL FORM OF TABLE 1

$$b_{i;0} = \frac{\sum_{j=1}^{11} y_{i,j}}{11} \text{ , } i=1,2,\ldots,9$$

$$b_{i;j} = \frac{\sum_{k=1}^{8} x_{j,k} \cdot y_{i,k}}{8} \text{ , } i=1,2,\ldots,9 \text{ , } j=1,2,3$$

$$b_{i;jk} = \frac{\sum_{l=1}^{8} x_{jk,l} \cdot y_{i,l}}{8} \text{ , } i=1,2,\ldots,9 \text{ , } j=1,2 \text{ , } k=j+1,\ldots,3$$

$$b_{i;11,22,33} = \frac{\sum_{j=1}^{8} y_{i,j}}{8} - \frac{\sum_{j=9}^{11} y_{i,j}}{3} \text{ , } i=1,2,\ldots,9$$

$$t.\sigma_{i;0} = t\,(\alpha=5\%,\nu=11)\,.\,\sigma\sqrt{\frac{1}{11}} \text{ , } i=1,2,\ldots,9 \text{ ; } t\,(\alpha=5\%,\nu=11) = 2.201$$

$$t.\sigma_{i;j} = t\,(\alpha=5\%,\nu=8)\,.\,\sigma\sqrt{\frac{1}{8}} \text{ , } i=1,2,\ldots,9 \text{ , } j=1,2,3 \text{ ; } t\,(\alpha=5\%,\nu=8) = 2.306$$

$$t.\sigma_{i;jk} = t\,(\alpha=5\%,\nu=8)\,.\,\sigma\sqrt{\frac{1}{8}} \text{ , } i=1,2,\ldots,9 \text{ , } j=1,2 \text{ , } k=i+1,\ldots,3 \text{ ; } t\,(\alpha=5\%,\nu=8) = 2.306$$

$$t.\sigma_{i;11,22,33} = t\,(\alpha=5\%,\nu=9)\,.\,\sigma\sqrt{\frac{1}{8}+\frac{1}{3}} \text{ , } i=1,2,\ldots,9 \text{ ; } t\,(\alpha=5\%,\nu=9) = 2.262$$

$$x_{ij,k} = x_{i,k} \cdot x_{j,k} \text{ , } i=1,2 \text{ , } j=i+1,\ldots,3 \text{ , } k=1,2,\ldots,11$$

$$\sigma = \sqrt{\frac{\sum_{j=9}^{11}\left(y_{i,j} - \frac{\sum_{k=9}^{11} y_{i,k}}{3}\right)}{2}}$$

FORMULAE UTILIZED TO GENERATE THE CANONICAL FORM OF TABLE 3

$$\left(\frac{\partial \hat{y}_i}{\partial x_{1,i}}\right)_{x_{2,i},x_{3,i}} \{x_{1,i}=x_{1,i,opt}\} = 2b_{11}\ x_{1,i,opt} + b_{12}\ x_{2,i} + b_{13}\ x_{3,i} + b_1 = 0 \text{ , } i=1,2,\ldots,9$$

$$\left(\frac{\partial \hat{y}_i}{\partial x_{2,i}}\right)_{x_{1,i},x_{3,i}} \{x_{2,i}=x_{2,i,opt}\} = b_{12}\ x_{1,i} + 2b_{22}\ x_{2,i,opt} + b_{23}\ x_{3,i} + b_2 = 0 \text{ , } i=1,2,\ldots,9$$

$$\left(\frac{\partial \hat{y}_i}{\partial x_{3,i}}\right)_{x_{1,i},x_{2,i}} \{x_{3,i}=x_{3,i,opt}\} = b_{13}\ x_{1,i} + b_{23}\ x_{2,i} + 2b_{33}\ x_{3,i,opt} + b_3 = 0 \text{ , } i=1,2,\ldots,9$$

$$\text{minimum: } \left(\frac{\partial^2 \hat{y}_i}{\partial x_{j,i}^2}\right)_{x_{k \neq j}} \{x_{j,i}=x_{j,i,opt}\} = 2b_{jj} > 0 \text{ , } i=1,2,\ldots,9 \text{ , } j=1,2,3$$

$$\text{maximum: } \left(\frac{\partial^2 \hat{y}_i}{\partial x_{j,i}^2}\right)_{x_{k \neq j}} \{x_{j,i}=x_{j,i,opt}\} = 2b_{jj} < 0 \text{ , } i=1,2,\ldots,9 \text{ , } j=1,2,3$$

$$\left(\frac{\partial \hat{y}_i}{\partial x_{1,i}}\right)_{x_{2,i},x_{3,i}} \{x_{1,i}=x_{1,i,Mopt}, x_{2,i}=x_{2,i,Mopt}, x_{3,i}=x_{3,i,Mopt}\} = 2b_{11}\ x_{1,i,Mopt} + b_{12}\ x_{2,i,Mopt} + b_{13}\ x_{3,i,Mopt} + b_1 = 0 \text{ , } i=1,2,\ldots,9$$

$$\left(\frac{\partial \hat{y}_i}{\partial x_{2,i}}\right)_{x_{1,i},x_{3,i}} \{x_{1,i}=x_{1,i,Mopt}, x_{2,i}=x_{2,i,Mopt}, x_{3,i}=x_{3,i,Mopt}\} = b_{12}\ x_{1,i,Mopt} + 2b_{22}\ x_{2,i,Mopt} + b_{23}\ x_{3,i,Mopt} + b_2 = 0 \text{ , } i=1,2,\ldots,9$$

$$\left(\frac{\partial \hat{y}_i}{\partial x_{3,i}}\right)_{x_{1,i},x_{2,i}} \{x_{1,i}=x_{1,i,Mopt}, x_{2,i}=x_{2,i,Mopt}, x_{3,i}=x_{3,i,Mopt}\} = b_{13}\ x_{1,i,Mopt} + b_{23}\ x_{2,i,Mopt} + 2b_{33}\ x_{3,i,Mopt} + b_3 = 0 \text{ , } i=1,2,\ldots,9$$

FORMULAE UTILIZED TO GENERATE THE CANONICAL FORM OF TABLE 2.

$$b_{i;0} = \frac{\sum_{j=1}^{19} y_{i,j}}{19} \text{ , } i=1,2,\ldots,9$$

$$b_{i;j} = \frac{\sum_{k=1}^{19} x_{j,k} \cdot y_{i,k}}{10} \text{ , } i=1,2,\ldots,9 \text{ , } j=1,2,3$$

$$b_{i;11} = \frac{19\left(\sum_{k=1}^{19} x_{1,k}{}^{2} . y_{i,k}\right) - 10\left(\sum_{k=1}^{19} y_{i,k}\right) - 52\, b_{i;22} - 52\, b_{i;33}}{90} \text{ , } i=1,2,\ldots,9$$

$$b_{i;22} = \frac{1{,}710\left(\sum_{k=1}^{19} x_{2,k}{}^{2} . y_{i,k}\right) - 988\left(\sum_{k=1}^{19} x_{1,k}{}^{2} . y_{i,k}\right) - 380\left(\sum_{k=1}^{19} y_{i,k}\right) - 1{,}976\, b_{i;33}}{1{,}976} \text{ , } i=1,2,\ldots,9$$

$$b_{i;33} = \frac{9{,}227{,}160\left(\sum_{k=1}^{19} x_{3,k}{}^{2} . y_{i,k}\right) - 3{,}378{,}960\left(\sum_{k=1}^{19} x_{2,k}{}^{2} . y_{i,k}\right) - 3{,}378{,}960\left(\sum_{k=1}^{19} x_{1,k}{}^{2} . y_{i,k}\right) - 1{,}299{,}600\left(\sum_{k=1}^{19} y_{i,k}\right)}{25{,}212{,}240} \text{ , } i=1,2,\ldots,9$$

$$b_{i;jk} = \frac{\sum_{l=1}^{8} x_{jk,l} \cdot y_{i,l}}{8} \text{ , } i=1,2,\ldots,9 \text{ , } j=1,2 \text{ , } k=j+1,\ldots,3$$

$$b_{i;111} = \frac{y_{i,15}-y_{i,14}}{2} - \frac{(y_{i,5}-y_{i,1}) + (y_{i,6}-y_{i,2}) + (y_{i,7}-y_{i,3}) + (y_{i,8}-y_{i,4})}{8} \text{ , } i=1,2,\ldots,9$$

$$b_{i;123} = \frac{\sum_{j=1}^{8} x_{123,j} \cdot y_{i,j}}{8} \text{ , } i=1,2,\ldots,9$$

$$b_{i;222} = \frac{y_{i,17}-y_{i,16}}{2} - \frac{(y_{i,3}-y_{i,1}) + (y_{i,4}-y_{i,2}) + (y_{i,7}-y_{i,5}) + (y_{i,8}-y_{i,6})}{8} \text{ , } i=1,2,\ldots,9$$

$$b_{i;333} = \frac{y_{i,19}-y_{i,18}}{2} - \frac{(y_{i,2}-y_{i,1}) + (y_{i,4}-y_{i,3}) + (y_{i,6}-y_{i,5}) + (y_{i,8}-y_{i,7})}{8} \text{ , } i=1,2,\ldots,9$$

$$B_{i,I \rightarrow II} = \frac{\sum_{j=12}^{13} y_j}{2} - \frac{\sum_{j=9}^{11} y_j}{3} \text{ , } i=1,2,\ldots,9$$

$$t.\sigma_{i;0} = t_{(\alpha=5\%, \nu=19)} \,.\, \sigma \sqrt{\frac{1}{19}} \text{ , } i=1,2,\ldots,9 \text{ , } j=1,2,3 \text{ ; } t_{(\alpha=5\%, \nu=19)} = 2.093$$

$$t.\sigma_{i;j} = t_{(\alpha=5\%, \nu=10)} \,.\, \sigma \sqrt{\frac{1}{10}} \text{ , } i=1,2,\ldots,9 \text{ , } j=1,2,3 \text{ ; } t_{(\alpha=5\%, \nu=10)} = 2.228$$

$$t.\sigma_{i;jj} = t_{(\alpha=5\%, \nu=10)} \,.\, \sigma \sqrt{\frac{1}{10}} \text{ , } i=1,2,\ldots,9 \text{ , } j=1,2,3 \text{ ; } t_{(\alpha=5\%, \nu=10)} = 2.228$$

$$t.\sigma_{i;jk} = t_{(\alpha=5\%, \nu=8)} \,.\, \sigma \sqrt{\frac{1}{8}} \text{ , } i=1,2,\ldots,9 \text{ , } j=1,2 \text{ , } k=i+1,\ldots,3 \text{ ; } t_{(\alpha=5\%, \nu=8)} = 2.306$$

$$t.\sigma_{i;jjj} = t_{(\alpha=5\%, \nu=8)} \,.\, \sigma \sqrt{\frac{1}{2} + \frac{1}{8}} \text{ , } i=1,2,\ldots,9 \text{ , } j=1,2,3 \text{ ; } t_{(\alpha=5\%, \nu=8)} = 2.306$$

$$t.\sigma_{i;123} = t_{(\alpha=5\%, \nu=8)} \,.\, \sigma \sqrt{\frac{1}{8}} \text{, } i=1,2,\ldots,9 \text{ ; } t_{(\alpha=5\%, \nu=8)} = 2.306$$

$$x_{ij,k} = x_{i,k} . x_{j,k} \text{ , } i=1,2 \text{ , } j=i+1,\ldots,3 \text{ , } k=1,2,\ldots,19$$

$$x_{123,i} = x_{1,i} . x_{2,i} . x_{3,i} \text{ , } i=1,2,\ldots,19$$

$$t.\sigma_{i;I \rightarrow II} = t_{(\alpha=5\%, \nu=3)} \,.\, \sigma \sqrt{\frac{1}{3} + \frac{1}{2}} \text{ , } i=1,2,\ldots,9 \text{ ; } t_{(\alpha=5\%, \nu=3)} = 3.182$$

$$\sigma = \sqrt{\frac{\sum_{j=9}^{13}\left(y_{i,j} - \frac{\sum_{k=9}^{13} y_{i,k}}{5}\right)}{4}}$$

CANONICAL FORM OF TABLE 1.

		E&I								MV CM				MVB				
	U	I	(1)	(2)	(3)	(12)	(13)	(23)	(11)+(22)+(33)	S	A	R	T	p	a	r	f	x
C	1	+1	$x_{1,1}$	$x_{2,1}$	$x_{3,1}$					$y_{1,1}$	$y_{2,1}$	$y_{3,1}$	$y_{4,1}$	$y_{5,1}$	$y_{6,1}$	$y_{7,1}$	$y_{8,1}$	$y_{9,1}$
	2	+1	$x_{1,2}$	$x_{2,2}$	$x_{3,2}$					$y_{1,2}$	$y_{2,2}$	$y_{3,2}$	$y_{4,2}$	$y_{5,2}$	$y_{6,2}$	$y_{7,2}$	$y_{8,2}$	$y_{9,2}$
	3	+1	$x_{1,3}$	$x_{2,3}$	$x_{3,3}$					$y_{1,3}$	$y_{2,3}$	$y_{3,3}$	$y_{4,3}$	$y_{5,3}$	$y_{6,3}$	$y_{7,3}$	$y_{8,3}$	$y_{9,3}$
	4	+1	$x_{1,4}$	$x_{2,4}$	$x_{3,4}$					$y_{1,4}$	$y_{2,4}$	$y_{3,4}$	$y_{4,4}$	$y_{5,4}$	$y_{6,4}$	$y_{7,4}$	$y_{8,4}$	$y_{9,4}$
	5	+1	$x_{1,5}$	$x_{2,5}$	$x_{3,5}$					$y_{1,5}$	$y_{2,5}$	$y_{3,5}$	$y_{4,5}$	$y_{5,5}$	$y_{6,5}$	$y_{7,5}$	$y_{8,5}$	$y_{9,5}$
	6	+1	$x_{1,6}$	$x_{2,6}$	$x_{3,6}$					$y_{1,6}$	$y_{2,6}$	$y_{3,6}$	$y_{4,6}$	$y_{5,6}$	$y_{6,6}$	$y_{7,6}$	$y_{8,6}$	$y_{9,6}$
	7	+1	$x_{1,7}$	$x_{2,7}$	$x_{3,7}$					$y_{1,7}$	$y_{2,7}$	$y_{3,7}$	$y_{4,7}$	$y_{5,7}$	$y_{6,7}$	$y_{7,7}$	$y_{8,7}$	$y_{9,7}$
	8	+1	$x_{1,8}$	$x_{2,8}$	$x_{3,8}$					$y_{1,8}$	$y_{2,8}$	$y_{3,8}$	$y_{4,8}$	$y_{5,8}$	$y_{6,8}$	$y_{7,8}$	$y_{8,8}$	$y_{9,8}$
c	9	+1	$x_{1,9}$	$x_{2,9}$	$x_{3,9}$					$y_{1,9}$	$y_{2,9}$	$y_{3,9}$	$y_{4,9}$	$y_{5,9}$	$y_{6,9}$	$y_{7,9}$	$y_{8,9}$	$y_{9,9}$
	10	+1	$x_{1,10}$	$x_{2,10}$	$x_{3,10}$					$y_{1,10}$	$y_{2,10}$	$y_{3,10}$	$y_{4,10}$	$y_{5,10}$	$y_{6,10}$	$y_{7,10}$	$y_{8,10}$	$y_{9,10}$
	11	+1	$x_{1,11}$	$x_{2,11}$	$x_{3,11}$					$y_{1,11}$	$y_{2,11}$	$y_{3,11}$	$y_{4,11}$	$y_{5,11}$	$y_{6,11}$	$y_{7,11}$	$y_{8,11}$	$y_{9,11}$
EE ±t.σ	S	$b_{1;0} \pm t.\sigma_{1;0}$	$b_{1;1} \pm t.\sigma_{1;1}$	$b_{1,2} \pm t.\sigma_{1,2}$	$b_{1,3} \pm t.\sigma_{1,3}$	$b_{1,12} \pm t.\sigma_{1,12}$	$b_{1,13} \pm t.\sigma_{1,13}$	$b_{1,23} \pm t.\sigma_{1,23}$	$b_{1;11,22,33} \pm t.\sigma_{1;11,22,33}$									
	A	$b_{2;0} \pm t.\sigma_{2;0}$	$b_{2;1} \pm t.\sigma_{2;1}$	$b_{2,2} \pm t.\sigma_{2,2}$	$b_{2,3} \pm t.\sigma_{2,3}$	$b_{2,12} \pm t.\sigma_{2,12}$	$b_{2,13} \pm t.\sigma_{2,13}$	$b_{2,23} \pm t.\sigma_{2,23}$	$b_{2;11,22,33} \pm t.\sigma_{2;11,22,33}$									
	R	$b_{3;0} \pm t.\sigma_{3;0}$	$b_{3;1} \pm t.\sigma_{3;1}$	$b_{3,2} \pm t.\sigma_{3,2}$	$b_{3,3} \pm t.\sigma_{3,3}$	$b_{3,12} \pm t.\sigma_{3,12}$	$b_{3,13} \pm t.\sigma_{3,13}$	$b_{3,23} \pm t.\sigma_{3,23}$	$b_{3;11,22,33} \pm t.\sigma_{3;11,22,33}$									
	T	$b_{4;0} \pm t.\sigma_{4;0}$	$b_{4;1} \pm t.\sigma_{4;1}$	$b_{4,2} \pm t.\sigma_{4,2}$	$b_{4,3} \pm t.\sigma_{4,3}$	$b_{4,12} \pm t.\sigma_{4,12}$	$b_{4,13} \pm t.\sigma_{4,13}$	$b_{4,23} \pm t.\sigma_{4,23}$	$b_{4;11,22,33} \pm t.\sigma_{4;11,22,33}$									
	p	$b_{5;0} \pm t.\sigma_{5;0}$	$b_{5;1} \pm t.\sigma_{5;1}$	$b_{5,2} \pm t.\sigma_{5,2}$	$b_{5,3} \pm t.\sigma_{5,3}$	$b_{5,12} \pm t.\sigma_{5,12}$	$b_{5,13} \pm t.\sigma_{5,13}$	$b_{5,23} \pm t.\sigma_{5,23}$	$b_{5;11,22,33} \pm t.\sigma_{5;11,22,33}$									
	a	$b_{6;0} \pm t.\sigma_{6;0}$	$b_{6;1} \pm t.\sigma_{6;1}$	$b_{6,2} \pm t.\sigma_{6,2}$	$b_{6,3} \pm t.\sigma_{6,3}$	$b_{6,12} \pm t.\sigma_{6,12}$	$b_{6,13} \pm t.\sigma_{6,13}$	$b_{6,23} \pm t.\sigma_{6,23}$	$b_{6;11,22,33} \pm t.\sigma_{6;11,22,33}$									
	r	$b_{7;0} \pm t.\sigma_{7;0}$	$b_{7;1} \pm t.\sigma_{7;1}$	$b_{7,2} \pm t.\sigma_{7,2}$	$b_{7,3} \pm t.\sigma_{7,3}$	$b_{7,12} \pm t.\sigma_{7,12}$	$b_{7,13} \pm t.\sigma_{7,13}$	$b_{7,23} \pm t.\sigma_{7,23}$	$b_{7;11,22,33} \pm t.\sigma_{7;11,22,33}$									
	f	$b_{8;0} \pm t.\sigma_{8;0}$	$b_{8;1} \pm t.\sigma_{8;1}$	$b_{8,2} \pm t.\sigma_{8,2}$	$b_{8,3} \pm t.\sigma_{8,3}$	$b_{8,12} \pm t.\sigma_{8,12}$	$b_{8,13} \pm t.\sigma_{8,13}$	$b_{8;23} \pm t.\sigma_{8;23}$	$b_{8;11,22,33} \pm t.\sigma_{8;11,22,33}$									
	x	$b_{9;0} \pm t.\sigma_{9;0}$	$b_{9;1} \pm t.\sigma_{9;1}$	$b_{9,2} \pm t.\sigma_{9,2}$	$b_{9,3} \pm t.\sigma_{9,3}$	$b_{9,12} \pm t.\sigma_{9,12}$	$b_{9,13} \pm t.\sigma_{9,13}$	$b_{9;23} \pm t.\sigma_{9;23}$	$b_{9;11,22,33} \pm t.\sigma_{9;11,22,33}$									

CANONICAL FORM OF TABLE 2.

		E&I									
	run	I	(1)	(2)	(3)	(11)	(22)	(33)	(12)	(13)	(23)
C	1	+1	$x_{1,1}$	$x_{2,1}$	$x_{3,1}$	$x_{11,1}$	$x_{22,1}$	$x_{33,1}$	$x_{12,1}$	$x_{13,1}$	$x_{23,1}$
	2	+1	$x_{1,2}$	$x_{2,2}$	$x_{3,2}$	$x_{11,2}$	$x_{22,2}$	$x_{33,2}$	$x_{12,2}$	$x_{13,2}$	$x_{23,2}$
	3	+1	$x_{1,3}$	$x_{2,3}$	$x_{3,3}$	$x_{11,3}$	$x_{22,3}$	$x_{33,3}$	$x_{12,3}$	$x_{13,3}$	$x_{23,3}$
	4	+1	$x_{1,4}$	$x_{2,4}$	$x_{3,4}$	$x_{11,4}$	$x_{22,4}$	$x_{33,4}$	$x_{12,4}$	$x_{13,4}$	$x_{23,4}$
	5	+1	$x_{1,5}$	$x_{2,5}$	$x_{3,5}$	$x_{11,5}$	$x_{22,5}$	$x_{33,5}$	$x_{12,5}$	$x_{13,5}$	$x_{23,5}$
	6	+1	$x_{1,6}$	$x_{2,6}$	$x_{3,6}$	$x_{11,6}$	$x_{22,6}$	$x_{33,6}$	$x_{12,6}$	$x_{13,6}$	$x_{23,6}$
	7	+1	$x_{1,7}$	$x_{2,7}$	$x_{3,7}$	$x_{11,7}$	$x_{22,7}$	$x_{33,7}$	$x_{12,7}$	$x_{13,7}$	$x_{23,7}$
	8	+1	$x_{1,8}$	$x_{2,8}$	$x_{3,8}$	$x_{11,8}$	$x_{22,8}$	$x_{33,8}$	$x_{12,8}$	$x_{13,8}$	$x_{23,8}$
c	9	+1	$x_{1,9}$	$x_{2,9}$	$x_{3,9}$	$x_{11,9}$	$x_{22,9}$	$x_{33,9}$	$x_{12,9}$	$x_{13,9}$	$x_{23,9}$
	10	+1	$x_{1,10}$	$x_{2,10}$	$x_{3,10}$	$x_{11,10}$	$x_{22,10}$	$x_{33,10}$	$x_{12,10}$	$x_{13,10}$	$x_{23,10}$
	11	+1	$x_{1,11}$	$x_{2,11}$	$x_{3,11}$	$x_{11,11}$	$x_{22,11}$	$x_{33,11}$	$x_{12,11}$	$x_{13,11}$	$x_{23,11}$
c	12	+1	$x_{1,12}$	$x_{2,12}$	$x_{3,12}$	$x_{11,12}$	$x_{22,12}$	$x_{33,12}$	$x_{12,12}$	$x_{13,12}$	$x_{23,12}$
	13	+1	$x_{1,13}$	$x_{2,13}$	$x_{3,13}$	$x_{11,13}$	$x_{22,13}$	$x_{33,13}$	$x_{12,13}$	$x_{13,13}$	$x_{23,13}$
ax	14	+1	$x_{1,14}$	$x_{2,14}$	$x_{3,14}$	$x_{11,14}$	$x_{22,14}$	$x_{33,14}$	$x_{12,14}$	$x_{13,14}$	$x_{23,14}$
	15	+1	$x_{1,15}$	$x_{2,15}$	$x_{3,15}$	$x_{11,15}$	$x_{22,15}$	$x_{33,15}$	$x_{12,15}$	$x_{13,15}$	$x_{23,15}$
	16	+1	$x_{1,16}$	$x_{2,16}$	$x_{3,16}$	$x_{11,16}$	$x_{22,16}$	$x_{33,16}$	$x_{12,16}$	$x_{13,16}$	$x_{23,16}$
	17	+1	$x_{1,17}$	$x_{2,17}$	$x_{3,17}$	$x_{11,17}$	$x_{22,17}$	$x_{33,17}$	$x_{12,17}$	$x_{13,17}$	$x_{23,17}$
	18	+1	$x_{1,18}$	$x_{2,18}$	$x_{3,18}$	$x_{11,18}$	$x_{22,18}$	$x_{33,18}$	$x_{12,18}$	$x_{13,18}$	$x_{23,18}$
	19	+1	$x_{1,19}$	$x_{2,19}$	$x_{3,19}$	$x_{11,19}$	$x_{22,19}$	$x_{33,19}$	$x_{12,19}$	$x_{13,19}$	$x_{23,19}$
EE ±t.σ	S	$b_{1;0}\pm t.\sigma_{1;0}$	$b_{1;1}\pm t.\sigma_{1;1}$	$b_{1;2}\pm t.\sigma_{1;2}$	$b_{1;3}\pm t.\sigma_{1;3}$	$b_{1;11}t.\sigma_{1;11}$	$b_{1;22}\pm t.\sigma_{1;22}$	$b_{1;33}\pm t.\sigma_{1;33}$	$b_{1;12}\pm t.\sigma_{1;12}$	$b_{1;13}\pm t.\sigma_{1;13}$	$b_{1;23}\pm t.\sigma_{1;23}$
	A	$b_{2;0}\pm t.\sigma_{2;0}$	$b_{2;1}\pm t.\sigma_{2;1}$	$b_{2;2}\pm t.\sigma_{2;2}$	$b_{2;3}\pm t.\sigma_{2;3}$	$b_{2;11}\pm t.\sigma_{2;11}$	$b_{2;22}\pm t.\sigma_{2;22}$	$b_{2;33}\pm t.\sigma_{2;33}$	$b_{2;12}\pm t.\sigma_{2;12}$	$b_{2;13}\pm t.\sigma_{2;13}$	$b_{2;23}\pm t.\sigma_{2;23}$
	R	$b_{3;0}\pm t.\sigma_{3;0}$	$b_{3;1}\pm t.\sigma_{3;1}$	$b_{3;2}\pm t.\sigma_{3;2}$	$b_{3;3}\pm t.\sigma_{3;3}$	$b_{3;11}\pm t.\sigma_{3;11}$	$b_{3;22}\pm t.\sigma_{3;22}$	$b_{3;33}\pm t.\sigma_{3;33}$	$b_{3;12}\pm t.\sigma_{3;12}$	$b_{3;13}\pm t.\sigma_{3;13}$	$b_{3;23}\pm t.\sigma_{3;23}$
	T	$b_{4;0}\pm t.\sigma_{4;0}$	$b_{4;1}\pm t.\sigma_{4;1}$	$b_{4;2}\pm t.\sigma_{4;2}$	$b_{4;3}\pm t.\sigma_{4;3}$	$b_{4;11}\pm t.\sigma_{4;11}$	$b_{4;22}\pm t.\sigma_{4;22}$	$b_{4;33}\pm t.\sigma_{4;33}$	$b_{4;12}\pm t.\sigma_{4;12}$	$b_{4;13}\pm t.\sigma_{4;13}$	$b_{4;23}\pm t.\sigma_{4;23}$
	p	$b_{5;0}\pm t.\sigma_{5;0}$	$b_{5;1}\pm t.\sigma_{5;1}$	$b_{5;2}\pm t.\sigma_{5;2}$	$b_{5;3}\pm t.\sigma_{5;3}$	$b_{5;11}\pm t.\sigma_{5;11}$	$b_{5;22}\pm t.\sigma_{5;22}$	$b_{5;33}\pm t.\sigma_{5;33}$	$b_{5;12}\pm t.\sigma_{5;12}$	$b_{5;13}\pm t.\sigma_{5;13}$	$b_{5;23}\pm t.\sigma_{5;23}$
	a	$b_{6;0}\pm t.\sigma_{6;0}$	$b_{6;1}\pm t.\sigma_{6;1}$	$b_{6;2}\pm t.\sigma_{6;2}$	$b_{6;3}\pm t.\sigma_{6;3}$	$b_{6;11}\pm t.\sigma_{6;11}$	$b_{6;22}\pm t.\sigma_{6;22}$	$b_{6;33}\pm t.\sigma_{6;33}$	$b_{6;12}\pm t.\sigma_{6;12}$	$b_{6;13}\pm t.\sigma_{6;13}$	$b_{6;23}\pm t.\sigma_{6;23}$
	r	$b_{7;0}\pm t.\sigma_{7;0}$	$b_{7;1}\pm t.\sigma_{7;1}$	$b_{7;2}\pm t.\sigma_{7;2}$	$b_{7;3}\pm t.\sigma_{7;3}$	$b_{7;11}\pm t.\sigma_{7;11}$	$b_{7;22}\pm t.\sigma_{7;22}$	$b_{7;33}\pm t.\sigma_{7;33}$	$b_{7;12}\pm t.\sigma_{7;12}$	$b_{7;13}\pm t.\sigma_{7;13}$	$b_{7;23}\pm t.\sigma_{7;23}$
	f	$b_{8;0}\pm t.\sigma_{8;0}$	$b_{8;1}\pm t.\sigma_{8;1}$	$b_{8;2}\pm t.\sigma_{8;2}$	$b_{8;3}\pm t.\sigma_{8;3}$	$b_{8;11}\pm t.\sigma_{8;11}$	$b_{8;22}\pm t.\sigma_{8;22}$	$b_{8;33}\pm t.\sigma_{8;33}$	$b_{8;12}\pm t.\sigma_{8;12}$	$b_{8;13}\pm t.\sigma_{8;13}$	$b_{8;23}\pm t.\sigma_{8;23}$
	x	$b_{9;0}\pm t.\sigma_{9;0}$	$b_{9;1}\pm t.\sigma_{9;1}$	$b_{9;2}\pm t.\sigma_{9;2}$	$b_{9;3}\pm t.\sigma_{9;3}$	$b_{9;11}\pm t.\sigma_{9;11}$	$b_{9;22}\pm t.\sigma_{9;22}$	$b_{9;33}\pm t.\sigma_{9;33}$	$b_{9;12}\pm t.\sigma_{9;12}$	$b_{9;13}\pm t.\sigma_{9;13}$	$b_{9;23}\pm t.\sigma_{9;23}$

CANONICAL FORM OF TABLE 2 (cont.).

		LoF					MV CM				MVB				
	run	(123)	(111)	(222)	(333)	block	S	A	R	T	p	a	r	f	x
C	1						$y_{1,1}$	$y_{2,1}$	$y_{3,1}$	$y_{4,1}$	$y_{5,1}$	$y_{6,1}$	$y_{7,1}$	$y_{8,1}$	$y_{9,1}$
	2						$y_{1,2}$	$y_{2,2}$	$y_{3,2}$	$y_{4,2}$	$y_{5,2}$	$y_{6,2}$	$y_{7,2}$	$y_{8,2}$	$y_{9,2}$
	3						$y_{1,3}$	$y_{2,3}$	$y_{3,3}$	$y_{4,3}$	$y_{5,3}$	$y_{6,3}$	$y_{7,3}$	$y_{8,3}$	$y_{9,3}$
	4						$y_{1,4}$	$y_{2,4}$	$y_{3,4}$	$y_{4,4}$	$y_{5,4}$	$y_{6,4}$	$y_{7,4}$	$y_{8,4}$	$y_{9,4}$
	5						$y_{1,5}$	$y_{2,5}$	$y_{3,5}$	$y_{4,5}$	$y_{5,5}$	$y_{6,5}$	$y_{7,5}$	$y_{8,5}$	$y_{9,5}$
	6						$y_{1,6}$	$y_{2,6}$	$y_{3,6}$	$y_{4,6}$	$y_{5,6}$	$y_{6,6}$	$y_{7,6}$	$y_{8,6}$	$y_{9,6}$
	7						$y_{1,7}$	$y_{2,7}$	$y_{3,7}$	$y_{4,7}$	$y_{5,7}$	$y_{6,7}$	$y_{7,7}$	$y_{8,7}$	$y_{9,7}$
	8						$y_{1,8}$	$y_{2,8}$	$y_{3,8}$	$y_{4,8}$	$y_{5,8}$	$y_{6,8}$	$y_{7,8}$	$y_{8,8}$	$y_{9,8}$
c	9						$y_{1,9}$	$y_{2,9}$	$y_{3,9}$	$y_{4,9}$	$y_{5,9}$	$y_{6,9}$	$y_{7,9}$	$y_{8,9}$	$y_{9,9}$
	10						$y_{1,10}$	$y_{2,10}$	$y_{3,10}$	$y_{4,10}$	$y_{5,10}$	$y_{6,10}$	$y_{7,10}$	$y_{8,10}$	$y_{9,10}$
	11						$y_{1,11}$	$y_{2,11}$	$y_{3,11}$	$y_{4,11}$	$y_{5,11}$	$y_{6,11}$	$y_{7,11}$	$y_{8,11}$	$y_{9,11}$
c	12						$y_{1,12}$	$y_{2,12}$	$y_{3,12}$	$y_{4,12}$	$y_{5,12}$	$y_{6,12}$	$y_{7,12}$	$y_{8,12}$	$y_{9,12}$
	13						$y_{1,13}$	$y_{2,13}$	$y_{3,13}$	$y_{4,13}$	$y_{5,13}$	$y_{6,13}$	$y_{7,13}$	$y_{8,13}$	$y_{9,13}$
ax	14						$y_{1,14}$	$y_{2,14}$	$y_{3,14}$	$y_{4,14}$	$y_{5,14}$	$y_{6,14}$	$y_{7,14}$	$y_{8,14}$	$y_{9,14}$
	15						$y_{1,15}$	$y_{2,15}$	$y_{3,15}$	$y_{4,15}$	$y_{5,15}$	$y_{6,15}$	$y_{7,15}$	$y_{8,15}$	$y_{9,15}$
	16						$y_{1,16}$	$y_{2,16}$	$y_{3,16}$	$y_{4,16}$	$y_{5,16}$	$y_{6,16}$	$y_{7,16}$	$y_{8,16}$	$y_{9,16}$
	17						$y_{1,17}$	$y_{2,17}$	$y_{3,17}$	$y_{4,17}$	$y_{5,17}$	$y_{6,17}$	$y_{7,17}$	$y_{8,17}$	$y_{9,17}$
	18						$y_{1,18}$	$y_{2,18}$	$y_{3,18}$	$y_{4,18}$	$y_{5,18}$	$y_{6,18}$	$y_{7,18}$	$y_{8,18}$	$y_{9,18}$
	19						$y_{1,19}$	$y_{2,19}$	$y_{3,19}$	$y_{4,19}$	$y_{5,19}$	$y_{6,19}$	$y_{7,19}$	$y_{8,19}$	$y_{9,19}$
EE $\pm t.\sigma$	S	$b_{1;123} \pm t.\sigma_{1;123}$	$b_{1;111} \pm t.\sigma_{1;111}$	$b_{1;222} \pm t.\sigma_{1;222}$	$b_{1;333} \pm t.\sigma_{1;333}$	$B_{1,I \to II} \pm t.\sigma_{1,I \to II}$									
	A	$b_{2;123} \pm t.\sigma_{2;123}$	$b_{2;111} \pm t.\sigma_{2;111}$	$b_{2;222} \pm t.\sigma_{2;222}$	$b_{2;333} \pm t.\sigma_{2;333}$	$B_{2,I \to II} \pm t.\sigma_{2,I \to II}$									
	R	$b_{3;123} \pm t.\sigma_{3;123}$	$b_{3;111} \pm t.\sigma_{3;111}$	$b_{3;222} \pm t.\sigma_{3;222}$	$b_{3;333} \pm t.\sigma_{3;333}$	$B_{3,I \to II} \pm t.\sigma_{3,I \to II}$									
	T	$b_{4;123} \pm t.\sigma_{4;123}$	$b_{4;111} \pm t.\sigma_{4;111}$	$b_{4;222} \pm t.\sigma_{4;222}$	$b_{4;333} \pm t.\sigma_{4;333}$	$B_{4,I \to II} \pm t.\sigma_{4,I \to II}$									
	p	$b_{5;123} \pm t.\sigma_{5;123}$	$b_{5;111} \pm t.\sigma_{5;111}$	$b_{5;222} \pm t.\sigma_{5;222}$	$b_{5;333} \pm t.\sigma_{5;333}$	$B_{5,I \to II} \pm t.\sigma_{5,I \to II}$									
	a	$b_{6;123} \pm t.\sigma_{6;123}$	$b_{6;111} \pm t.\sigma_{6;111}$	$b_{6;222} \pm t.\sigma_{6;222}$	$b_{6;333} \pm t.\sigma_{6;333}$	$B_{6,I \to II} \pm t.\sigma_{6,I \to II}$									
	r	$b_{7;123} \pm t.\sigma_{7;123}$	$b_{7;111} \pm t.\sigma_{7;111}$	$b_{7;222} \pm t.\sigma_{7;222}$	$b_{7;333} \pm t.\sigma_{7;333}$	$B_{7,I \to II} \pm t.\sigma_{7,I \to II}$									
	f	$b_{8;123} \pm t.\sigma_{8;123}$	$b_{8;111} \pm t.\sigma_{8;111}$	$b_{8;222} \pm t.\sigma_{8;222}$	$b_{8;333} \pm t.\sigma_{8;333}$	$B_{8,I \to II} \pm t.\sigma_{8,I \to II}$									
	x	$b_{9;123} \pm t.\sigma_{9;123}$	$b_{9;111} \pm t.\sigma_{9;111}$	$b_{9;222} \pm t.\sigma_{9;222}$	$b_{9;333} \pm t.\sigma_{9;333}$	$B_{9,I \to II} \pm t.\sigma_{9,I \to II}$									

CANONICAL FORM OF TABLE 3.

		LO			**TO**			**MM**		
		x_1	x_2	x_3	x_1	x_2	x_3	x_1	x_2	x_3
EE	**S**	$x_{1,1,opt}$	$x_{2,1,opt}$	$x_{3,1,opt}$				$x_{1,1,Mopt}$	$x_{2,1,Mopt}$	$x_{3,1,Mopt}$
	A	$x_{1,2,opt}$	$x_{2,2,opt}$	$x_{3,2,opt}$				$x_{1,2,Mopt}$	$x_{2,2,Mopt}$	$x_{3,2,Mopt}$
	R	$x_{1,3,opt}$	$x_{2,3,opt}$	$x_{3,3,opt}$				$x_{1,3,Mopt}$	$x_{2,3,Mopt}$	$x_{3,3,Mopt}$
	N	$x_{1,4,opt}$	$x_{2,4,opt}$	$x_{3,4,opt}$				$x_{1,4,Mopt}$	$x_{2,4,Mopt}$	$x_{3,4,Mopt}$
	p	$x_{1,5,opt}$	$x_{2,5,opt}$	$x_{3,5,opt}$				$x_{1,5,Mopt}$	$x_{2,5,Mopt}$	$x_{3,5,Mopt}$
	a	$x_{1,6,opt}$	$x_{2,6,opt}$	$x_{3,6,opt}$				$x_{1,6,Mopt}$	$x_{2,6,Mopt}$	$x_{3,6,Mopt}$
	r	$x_{1,7,opt}$	$x_{2,7,opt}$	$x_{3,7,opt}$				$x_{1,7,Mopt}$	$x_{2,7,Mopt}$	$x_{3,7,Mopt}$
	f	$x_{1,8,opt}$	$x_{2,8,opt}$	$x_{3,8,opt}$				$x_{1,8,Mopt}$	$x_{2,8,Mopt}$	$x_{3,8,Mopt}$
	x	$x_{1,9,opt}$	$x_{2,9,opt}$	$x_{3,9,opt}$				$x_{1,9,Mopt}$	$x_{2,9,Mopt}$	$x_{3,9,Mopt}$

REFERENCES

ADAMS, M.R. and HALL, C.J. 1988. Growth inhibition of food-borne pathogens by lactic and acetic acid and their mixtures. Int. J. Food Sci. Technol. *23*, 287-292.

ANDERSSON, R.E., ERIKSSON, C.E., SALOMONSSON, A.C. and THEANDE, O. 1990. Lactic acid fermentation of fresh and stored carrot: chemical, microbial and sensory evaluation of products. Lebensmitt. Wiss. u-Technol. *23*, 34-40.

BELL, T., TURNEY, L. and ETCHELLS, J. 1972. Influence of different organic acids on firmness of fresh-packed pickles. J. Food Sci. *37*, 446-449.

BERGEY, D. H. 1989. *Bergey's Manual of Systematic Bacteriology*. p. 1229. Williams and Wilkins, Baltimore.

BINSTED, R., DEVEY, J. D. and DAKIN, J. C. 1962. *Pickle and Sauce Making*. p. 106. Food Trade, London.

BOX, G.E.P., HUNTER, W.G. and HUNTER, J.S. 1978. *Statistics for Experimenters*. John Wiley & Sons, New York.

DIEZ, M.J., *et al.* 1985. *Biotecnologia de la Aceituna de Mesa*. Instituto de la Grasa. Sevilla.

ETCHELLS, M., BELL, T.A., FLEMING, H. and POTTS, E. 1973. Suggested procedure for the controlled fermentation of commercially brined pickling cucumbers - use of starter cultures and reduction of carbon dioxide accumulation. Pickle Pak. Sci. *3*, 4-14.

FLEMING, H.P. 1982. Fermented vegetables. In *Economic Microbiology and Fermented Food*. p. 277, (A.H. Rose, ed.) Academic Press, New York.

FLEMING, H.P., McFEETERS, R., THOMPSON, R. and SANDERS, D. 1983. Storage stability of vegetables fermented with pH control. J. Food Sci. *49*, 975-981.

McKNEE, J.M.T. 1985. A single method for the extraction of reducing sugars and nonreducing sugars from carrots and other storage vegetables. J. Sci. Food Agric. *36*, 55-58.

MOREIRA, L.A., OLIVEIRA, F.A.R. and SILVA, T.R. 1992. Prediction of pH change in processed acidified turnips. Int. J. Food Sci. Technol. *57*, 928-931.

NABAIS, R.M., and MALCATA, F.X. 1995. Modelling the transport of lactic acid, sodium chloride and reducing sugars in carrot slices submerged in carrot slices submerged in brines. Part 2: Multivariate approach. J. Food Eng. In Press.

NABAIS, R.M., VIEIRA, M.C. and MALCATA, F.X. 1995. J. Food Eng. Modelling the transport of lactic acid, sodium chloride and reducing sugars in carrot slices submerged in brines. Part I: Multivariate approach. In Press.

NIKETIC-ALEKSIC, G.K., BOURNE, M.C. and STAMER, J.R. 1973. Preservation of carrots by lactic acid fermentation. J. Food Sci. *38*, 84-86.

SCHWARTZBERG, H.B. and CHAO, R.Y. 1982. Solute diffisivities in leaching processes. Food Technol. *36*, 73-86.

STEINKRAUS, K.H. 1983. Acid fermented vegetables. In *Handbook of Indigenous Fermented Food Involving an Acid Fermentation*, p. 127, Marcel Dekker, New York.

INFLUENCE OF BLANCHING TREATMENTS ON THE TEXTURE AND COLOR OF SOME PROCESSED VEGETABLES AND FRUITS

ZHIMIN LIN[1,3] and EUGENE SCHYVENS[2]

[1]*Department of Biotechnology and Food Science*
Yi Yuan 22-106, Fuzhou University
Fuzhou, 350002, P.R. China
[2]*Agrotechnological Research Institute*
Wageningen, The Netherlands

Accepted for Publication July 31, 1995

ABSTRACT

Fifteen selected vegetables and fruits were processed by conventional procedures with modified blanching conditions. The texture of blanched and processed samples was determined. Low-Temperature-Long-Time (LTLT) blanching considerably increased the final firmness of sterilized carrot, endive and green bean samples, as well as pasteurized cherry samples. After screening experiments, green bean and endive were chosen for further research. Analysis of variance revealed that LTLT blanching treatments in a blanching solution containing calcium and zinc cation significantly affected the texture and color of processed green bean and endive. The blanching treatments were optimized to improve the texture and color of sterilized green bean and endive.

INTRODUCTION

Texture is one of the most important quality attributes affecting the acceptability of processed vegetables and fruits. However, processed vegetables and fruits may become excessively soft after processing, especially sterilized low-acid products.

Previous studies have shown that Low-Temperature-Long-Time (LTLT) blanching improved final firmness of a few processed vegetables and fruits by xxx

---

[3]To whom correspondence should be sent.

Journal of Food Processing and Preservation **19**(1995) 451–465. *All Rights Reserved*

activating native Pectin Methyl Esterase (PME) in the tissue of those products. Pala (1983) indicated that the maximum firmness of frozen carrot could be obtained by LTLT blanching at 70C for 15 min followed by High-Temperature-Short-Time (HTST) blanching. Addition of calcium to blanching water further improved the texture. Quintero-Ramos (1992) reported that the firmness of rehydrated product of dried carrot could be significantly increased when carrot were blanched at 60–65C for more than 30 min. Steinbuch (1976) discovered that a heat pretreatment at 75C for 5 min before HTST blanching for frozen green bean resulted in maximal increase of hardness. In addition, Alonso (1993) reported the final texture of frozen cherries could be significantly improved by low temperature heating at 70C before freezing.

We hypothesized that other vegetables and fruits also have PME activity and that their texture could be improved by LTLT blanching. Furthermore, we hypothesized that LTLT blanching may not only enhance the firmness of frozen products but also sterilized or pasteurized products.

When LTLT blanching was employed to enhance the firmness for some green vegetables, this process also adversely affected the color of green vegetables. The unattractive olive-green color caused by LTLT blanching was in sharp contrast to the bright-green color of HTST blanched samples. Although this difference in color was eliminated after canning, it remained a critical factor affecting the acceptability of frozen products.

The major reason for the color change is the formation of pheophytins from chlorophyll, which is caused by hydrogen replacing magnesium in the chlorophyll molecule. Prior process for the retention of green color in canned green vegetables required a chemical additive to achieve color retention. These additives may be classified into 2 groups: (1) alkalizing or alkalizing-buffer agents such as the hydroxides or carbonates (Malecki 1964; Gupte *et al.* 1961) and (2) metallic salts such as the chlorides and acetates of zinc and copper (Schanderl *et al.* 1966; Jones *et al.* 1977; Von Elbe 1989) . The drawback in the utilization of alkalizing agents for the retention of color in canned green vegetables is that the intensity of the remained green color decreases gradually when the canned green vegetable is kept in storage at room temperature. In contrast, the zinc ion replacing the magnesium in the chlorophyll molecule may result in a stable green compound. In addition, nutritional surveys of adults indicated that the intake of zinc generally falls below the RDA (Recommended Dietary Allowances) for all age and sex categories (Segner *et al.* 1984).

Therefore, we chose zinc salt as an additive into the blanching water for the color retention of processed green vegetables. We hypothesized that the green color would be affected by not only the blanching condition, but also the concentration of zinc cation. The addition of zinc cation into blanching water might improve the color of frozen vegetables as well as sterilized vegetables.

MATERIALS AND METHODS

Raw Materials

Vegetables and fruits were purchased from a local firm (Wageningen, The Netherlands) and placed in cold store. The cultivars of vegetables and fruits were unknown with the exception that the cultivar of green bean was Masai.

Processing Procedures

In the screening experiments, 15 kinds of vegetables and fruits, i.e., carrot, beetroot, leek, endive, celery, rhubarb, onion, spinach, red cabbage, white cabbage, cucumber, green bean, cherry, apple and pear were selected for experiments. Conventional processing procedures were employed for each selected vegetable and fruit with the exception that blanching conditions were modified. Blanching treatments were also applied for fruits. After washing, peeling, coring, slicing, etc., samples were blanched at 50, 60, 70, 80 C, respectively, for 10 min in a steam jacketed kettle, cooled in tap water and drained. The drained samples were filled into jars (370 ml) and brine or sugar solution was added. After that, the jars were steam closed. Finally, the jars were sterilized (110-118C for 25-70 min) in a still retort or pasteurized (80-100C for 18-45 min) in a pasteurizer according to conventional processing temperatures and times. Then the jars were cooled to 20C and stored at 15C.

After screening experiments, it was found that LTLT blanching considerably increased the final firmness of sterilized carrot, endive and green bean samples, as well as pasteurized cherry sample. Since the facts that endive has PME activity and the texture of sterilized green bean may be improved by LTLT blanching have not been reported in literatures, green bean and endive were chosen for further research.

In further research, conventional processing procedures were also used for green bean and endive. Blanching conditions for sterilized samples were modified as described in experimental design. Frozen samples were also LTLT blanched as sterilized samples, followed by HTST blanching to inactivate enzymes. Green bean and endive were frozen at -40C for 2 h and stored at -23C.

Experimental Design

Experimental design of 4 factors and 3 levels was arranged for blanching treatments of green bean and endive. Orthogonal experiments design was applied to these experiments (Table 1).

TABLE 1.
EXPERIMENTAL DESIGN OF BLANCHING CONDITIONS
FOR PROCESSED GREEN BEAN AND ENDIVE

Factors	Green Bean			Endive		
Blanching Temperature (℃)	60	65	70	50	55	60
Blanching Time (min)	5	10	15	4	8	12
Concentration of Ca^{++} (ppm)	0	400	800	0	400	800
Concentration of Zn^{++} (ppm)	0	100	200	0	100	200

Measurements of Firmness and Color for the Samples

In the screening experiments, the firmness of blanched, sterilized or pasteurized samples was measured by an Instron Universal Testing Machine (IUTM) after processing. Some pasteurized samples to which high concentration of sugar solution was added, such as cherry, rhubarb, etc. were measured after 3 weeks storage.

In the second-stage experiments, the firmness of sterilized samples and frozen samples was measured by IUTM. The color of the same samples was tested by Computer Image System (CIS) and Minolta Instrument (MI), respectively.

Firmness Measurement of the Samples. Samples were drained and mixed. The frozen green bean sample was cooled at 100C for 12 min and cooked by tap water. The frozen endive sample was heated to 80C and cooled by icy water.

Firmness was measured by placing a 40 g well drained and mixed sample into the shear cell. Four measurements were made per sample. The Top Force (N) of the sample tested by 1UTM was used to represent the firmness of the sample.

Color Measurement of the Samples. CIS was calibrated with red and green standard plate affiliated to MI for color measurement of green bean samples. Four pieces of drained green bean were selected randomly for color measurement by CIS. The color measurement for each sample was repeated 10 times. Then the same 10 groups of 4 pieces of green bean were placed on a black board, and each group of green bean sample was measured by MI 2 times at different positions.

For the color measurements of endive samples, CIS was calibrated with special red and green plate prepared by a professional researcher. The drained endive sample was separated onto 3 glass dishes. The endive in each dish was measured by CIS. The color measurement for each sample was repeated 3 times. After that, each dish of endive was measured by MI 5 times at different positions.

Gold and Weckel (1959) found a high linear correlation between the value of -a/b and the degree of conversion from chlorophyll to pheophytin. Thus, the L, a, b values measured by CIS were used to describe the color of samples, and compared with those tested by MI.

Statistical Analysis

The measurement data of these samples were calculated by Genstat 5 statistical package for analysis of variance.

RESULTS AND DISCUSSION

The Results of Screening Experiments

The results of screening experiments revealed that among 15 selected vegetables and fruits samples, LTLT blanching considerably increased the final firmness of sterilized carrot, endive and green bean samples, as well as pasteurized cherry sample (Fig. 1, 2, 3, 4).

From Fig. 1, it could be estimated the optimal LTLT blanching temperature might be 60-70C for textural improvement of sterilized carrot. Similarly, the optimal LTLT blanching temperature might be 50-60C, 60-70C for sterilized endive and green bean, respectively.

From Fig. 4, it could be estimated the optimal LTLT blanching temperature might be 60-70C for textural improvement of pasteurized cherry. Unexpectedly, the pasteurized cherry samples were firmer than blanched samples. Probably this was caused by infiltration of high concentration of sugar solution into the tissue of cherry samples.

The Results and Analysis of Second-Stage Experiments

In the second-stage experiments, effect of modified LTLT blanching treatments on the texture and color of processed green bean and endive were investigated.

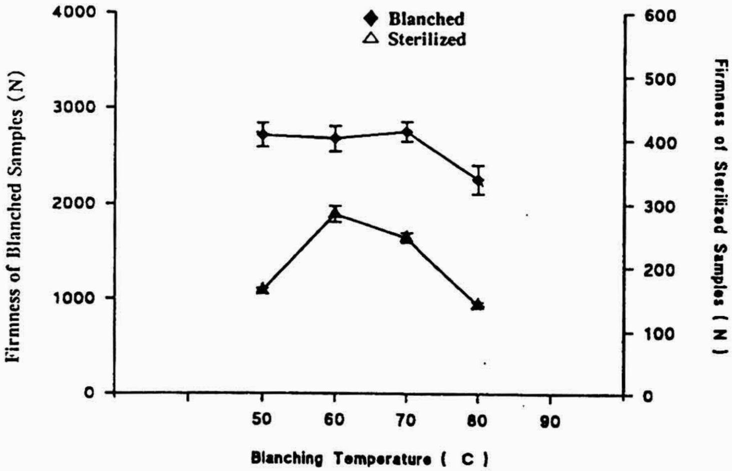


FIG. 1. FIRMNESS OF CARROT SAMPLES AFTER DIFFERENT TREATMENTS

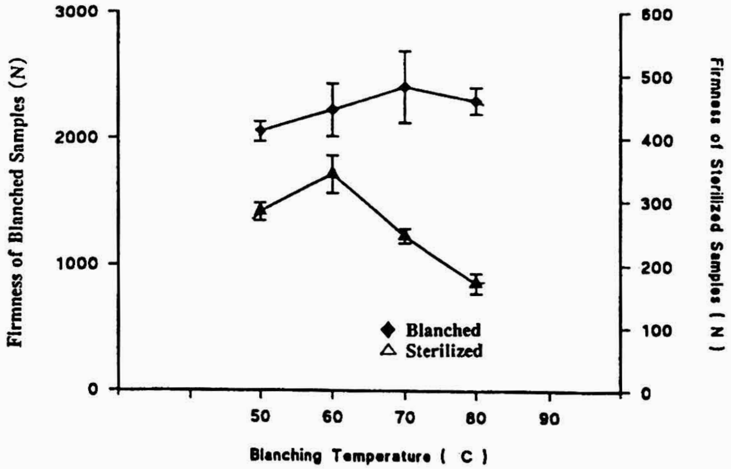


FIG. 2. FIRMNESS OF ENDIVE SAMPLES AFTER DIFFERENT TREATMENTS

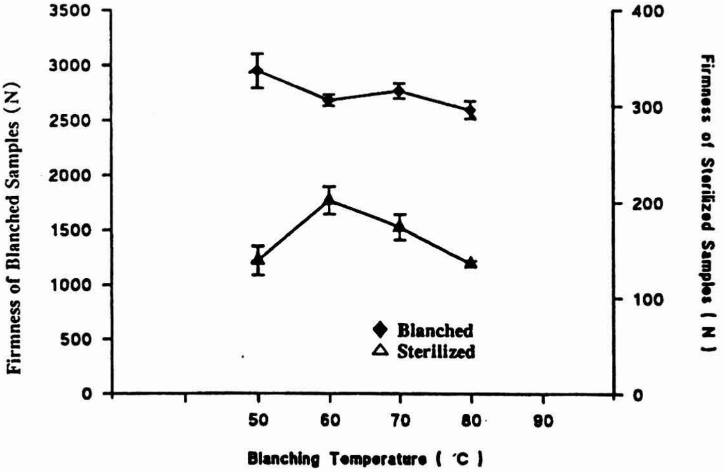


FIG.3.FIRMNESS OF GREEN BEAN SAMPLES AFTER DIFFERENT TREATMENTS

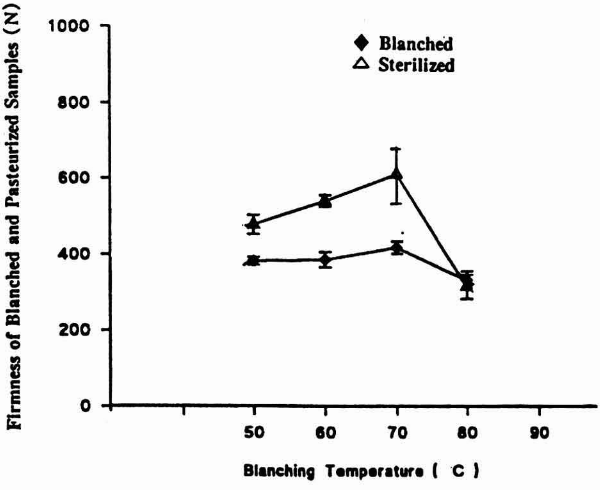


FIG.4. FIRMNESS OF CHERRY SAMPLES AFTER DIFFERENT TREATMENTS

Analysis of variance for measurement data revealed that blanching temperature, blanching time and calcium concentration significantly influenced the firmness of sterilized green bean at 0.001, less than 0.001, and 0.011 level, respectively. Whereas for frozen green bean after cooking, only blanching time significantly affected the firmness at 0.003 level (Table 2).

TABLE 2.
ANALYSIS OF VARIANCE FOR EFFECT OF FACTORS ON FIRMNESS OF PROCESSED GREEN BEAN

Factors	Firmness (N)	
	Sterilized	Frozen
Temp. (C)		
60	243.0 A	
65	225.8 B	
70	223.2 B	
Time (min)		
5	214.9 C	692 C
10	227.8 B	840 B
15	249.2 A	969 A
Ca^{++} (ppm)		
0	222.5 B	
400	233.8 A	
800	235.5 A	

Values are means and values on the same column followed by same letter(s) are not significantly different (a=0.05)

Apparently, blanching time was the most important factor affecting the firmness of sterilized green bean, whereas blanching temperature was the secondary factor and calcium cation was the third factor. It seemed that the optimam blanching condition to improve the texture of sterilized green bean might be 60C, 15 min in blanching solution containing 400 ppm Ca^{++}.

Analysis of variance for measurement data showed that blanching temperature and blanching time significantly affected the firmness of sterilized endive at less than 0.001 and 0. 007 level, respectively (Table 3). In contrast to sterlized green bean, Ca^{++} concentration had no significant influence on the firmness of sterilized endive. A plausible explanation is that native calcium in endive was sufficient to tie up the available carboxyl groups resulting from de-esterification of pectin molecules in the cell wall. Thus the effect of added calcium cation in blanching water was negligible. For frozen endive after heating, only blanching temperature significantly affected the firmness at 0.005 level (Table 3).

TABLE 3.
ANALYSIS OF VARIANCE FOR EFFECTOF FACTORS
ON FIRMNESS OF PROCESSED ENDIVE

Factors	Firmness (N)	
	Sterilized	Frozen
Temp. (C)		
50	265.3 C	1191 B
55	299.8 B	1324 B
60	340.6 A	1915 A
Time (min)		
5	277.3 B	
8	315.3 A	
12	313.1 A	

Values are means and values on the same column followed by same letter(s) are not significantly different (a=0.05)

Obviously, blanching temperature was the main factor that influenced the firmness of sterilized endive, while blanching time was the secondary factor. It seemed that the optimal blanching condition for textural improvement of sterilized endive might be 60C for 8 min.

Both sterilized green bean and endive had the same optimum blanching temperature, i.e., 60C, to improve the firmness retention. The difference of optimum blanching time between sterilized green bean and endive was probably caused by heat transfer. Green bean are thicker than endive, therefore more time should be consumed for heat penetration to the center of green bean than to that of endive.

As mentioned above, the most important factor affecting the firmness of sterilized green bean was blanching time, which was also the only factor significantly enhancing the firmness of frozen green bean after cooking. Similarly, the main factor affecting the firmness of sterilized endive was blanching temperature, which was also the only factor significantly improving the firmness of frozen endive after heating. The plausible explanation may be that the firmness of processed vegetables is much greater by freezing preservation than by the sterilization process. Thus, only the factor which most significantly influenced the firmness of sterilized vegetables could have some effect on the firmness of frozen products.

Blanching temperature and Zn^{++} concentration significantly affected the color of sterilized green bean at less than 0.001 level, respectively. In addition, interaction between blanching temperature and blanching time on the color of sterilized green bean was detected at 0.036 significant level (Table 4).

TABLE 4.
ANALYSIS OF VARIANCE FOR EFFECT OF FACTORS
ON COLOR OF STERILIZED GREEN BEAN

Temp. (C)	Color (−a/b)	Zn^{++} (ppm)	Color (−a/b)
60	0.7487 A	0	0.7127 C
65	0.7296 B	100	0.7252 B
70	0.7052 C	200	0.7456 A

Interaction between blanching temperature and blanching time
(−a/b)

Blanching Time / Blanching Temp.	60 C	65 C	70 C
5 min	0.7501 A	0.7275 A	0.6912 B
10 min	0.7490 A	0.7398 A	0.7042 AB
15 min	0.7470 A	0.7216 A	0.7203 A

Values are means and values on the same column followed by same letter(s) are not significantly different (a=0.05)

Apparently, blanching temperature and Zn^{++} concentration were main factors affecting the color of sterilized green bean, whereas the interaction between blanching temperature and blanching time was the secondary factor. According to main factors, it seemed that green bean should be blanched at 60C in blanching solution containing 200 ppm Zn^{++} to improve color retention. Further analysis of Least Significant Difference (LSD) revealed that only when blanching temperature was 70C, the interaction between blanching temperature and blanching time significantly influenced the color of sterilized green bean. Thus, when blanching temperature is fixed at 60C, the interaction may be neglected.

For frozen green bean after cooking, blanching temperature, blanching time and Zn^{++} concentration significantly influenced the color at less than 0.001, 0.002 and 0.027 level, respectively (Table 5).

TABLE 5.
ANALYSIS OF VARIANCE FOR EFFECT OF FACTORS
ON COLOR OF FROZEN GREEN BEAN

Temp. (C)	Color (−a/b)		Time (min)	Color (−a/b)		Zn^{++} (ppm)	Color (−a/b)	
60	0.8357	A	5	0.8456	A	0	0.8014	B
65	0.8369	A	10	0.8126	B	100	0.8243	A
70	0.7825	B	15	0.7968	B	200	0.8294	A

Values are means and values on the same column followed by same letter(s) are not significantly different (a=0.05)

Blanching temperature and Zn^{++} concentration significantly affected the color of sterilized endive at 0.002 and less than 0.001 level, respectively. For frozen endive after heating, only blanching temperature significantly affected the color at less than 0.001 (Table 6).

TABLE 6.
ANALYSIS OF VARIANCE FOR EFFECT OF FACTORS
ON COLOR OF PROCESSED ENDIVE

Factors	Color (−a/b)			
	Sterilized		Frozen	
Temp. (C)				
50	0.1767	A	0.559	B
55	0.1105	B	0.604	B
60	0.1327	B	0.772	A
Zn^{++} (ppm)				
0	0.0887	C		
100	0.1436	B		
200	0.1876	A		

Values are means and values on the same column followed by same letter(s) are not significantly different (a=0.05)

Evidently, zinc cation concentration was the main factor affecting the color of sterilized endive and blanching temperature was the secondary factor. It seemed that the optimum blanching condition to improve the color of sterilized endive might be 50C in blanching solution containing 200 ppm Zn^{++}.

The concentration of Zn^{++} in blanching water significantly influenced the color of sterilized green bean and endive, the higher the concentration of zinc cation, the better the color retention. However, it seemed that the concentration of Zn^{++} in blanching water had less effect on the color of frozen bean and even no effect on the color of frozen endive. The probable reason may be that green vegetables may have much better color retention by freezing preservation than by sterilization process. Therefore, the effect of Zn^{++} on the color retention of frozen vegetables may be reduced and even negligible.

If both the testure and color of sterilized green bean are taken into account, probably the optimum blanching condition should be 60C, 15 min in blanching solution containing 400 ppm Ca^{++} and 200 ppm Zn^{++}.

If both the texture and color of sterilized endive are taken into account, since blanching temperature was the main factor affecting the firmness of sterilized endive and the secondary factor influencing the color of sterilized endive, it should be given priority over blanching temperature even though blanching temperature had conflicting influence on the the firmness and color retention for sterilized endive. It might be reasonable that optimal blanching condition should be 60C, 8 min in blanching solution containing 200 ppm Zn^{++}.

Finally, the color data for the same products measured by MI (data not shown) were compared with those tested by CIS. After comparison by analysis of variance for data measured by MI and CIS, it seemed that the data tested by MI and those by CIS were comparable and they resulted in similar consequences. However, CIS was all-inclusive and more exact and sensitive. The plausible explanation might be that CIS may measure the color of the whole surface of the object while MI can only measure the color of some points on the surface of the object. The advantage of CIS was apparent, especially when both MI and CIS were used to measure the color of endive samples as the endive sample in fact was a mixture containing green leaves and white stems.

The Results of Confirmative Experiments

On the basis of the above analysis and discussion, the optimum LTLT blanching conditions for sterilized green bean and endive were confirmed. The results of confirmative experiments are showen in Table 7. In addition, the results of controls processed by conventional blanching treatments are shown in Table 8.

TABLE 7.
RESULTS OF CONFIRMATIVE EXPERIMENTS FOR
STERILIZED GREEN BEAN AND ENDIVE

Products	LTLT Blanching Conditions				Measurement Results	
	Temp. (℃)	Time (min)	Ca^{++} (ppm)	Zn^{++} (ppm)	Firmness (N)	Color (−a/b)
Green Bean	60	15	400	200	275. 8	0. 768351
Endive	60	8	0	200	365. 5	0. 174832

TABLE 8.
MEASUREMENT RESULTS OF THE CONTROLS

Products	Conventional Blanching		Measurement Results	
	Temp. (℃)	Time (min)	Firmness (N)	Color (−a/b)
Green Bean	90	3	123. 5	0. 693811
Endive	95	6	196. 8	0. 0578138

By comparision of the above 2 tables, it could be seen that the texture and color of sterlized green bean and endive treated by optimum LTLT blanching were much better than those treated by conventional blanching.

CONCLUSION

LTLT blanching treatment may be utilized to improve the texture of some processed vegetables and fruits, especially the firmness of a few processed vegetables and fruit such as carrot, green bean, endive and cherry, by activating native PME in the tissue of those products.

Optimized blanching treatments may be employed to improve both texture and color of sterilized greeen bean and endive. The research results indicated both blanching temperature and blanching time significantly affected the firmness of sterilized green bean and endive. However, the main factor affecting the texture of sterilized green bean was blanching time, which was also the only factor enhancing the firmness of frozen green bean after cooking. The main factor influencing the texture of sterilized endive was blanching temperature, which was also the only factor increasing the firmness of frozen endive after heating. The addition of a certain amount of calcium cation to blanching water significantly influenced the texture of sterilized green bean, but did not significantly affected the firmness of sterilized endive. Zinc cation concentration added in blanching water greatly affected the color of sterilized grean bean and endive, but had less effect on the color of frozen green bean after cooking, and no effect on the color of frozen endive after heating.

CIS is better than MI in measuring color of green bean and endive samples and may have good prospect in the future.

ACKNOWLEGMENTS

Thanks to T. Timmermans for his assistance in color measurements of the samples by CIS.

REFERENCES

ALNOSO, J., CANET, W. and RODRIGUEZ, M.T. 1993. Effect of various thermal pre-treatments on the texture of frozen cherries (*Prunus avium* L.) Related enzyme activities. Z Lebensm Unters Forsch *196*, 211–218.

GUPTE, S.M. and FRANCIS, F.J. 1964. Effect of PH adjustment and high temperature short time processing on color and pigment retention in spinach puree. Food Technol. *18*, 1645.

GOLD, H.J. and WECKEL, K.G. 1959. Degradation of chlorophyll to pheophytin during sterilization of canned green peas by heat. Food Technol. *13*(5), 281–286

JONES, I.D., WHITE, R.C., GIBBS, E., BUTLER, L.S. and NELSON, L.A. 1977. Experimental formation of zinc and copper complexes of cholorophyll derivation in vegetable tissue by thermal processing. J. Agri. Food Chem. *25*, 1.

MALECKI, G.J. 1964. Retains vegetable green. Food Eng. *37*(6), 93.

PALA, M. 1983. Stepwise blanching and its importance in freezing of vegetables. *Refrigeration in the Service of Man*. Vol. 3, 631-638, XVIth International Congress of Refrigeration. Paris.

QUINTERO-RAMOS, A., BOURNE, M.C. and ANZALDUA-MORALES, A. 1992. Texture and rehydration of dehydrated carrots as affected by low temperature blanching. J Food Sci. *67*(6), 1127-1128.

/ STEINBUCH, E. 1976. Improvement of texture of frozen vegetables by stepwise blanching treatments. J. Food Technol. *11*, 313-316.

SCHANDERL, S.H., MARSH, G.L. and CHICHESTER, C.O. 1965. Color reversion in processed vegetables, I. Studies on regreen pea puree. J. Food Sci. *27*, 3865.

SEGNER, W.P., RAGUSA, T.J., NANR, W.K. and HOYLE, W.C. 1984. Process for the preservation of green color in canned vegetables. United States patent 4473591.

VON ELBE, J.H. 1989. Improving the color of canned green vegetables. Food Beverage Technol. Int. p. 243.

MATHEMATICAL MODELLING OF MOISTURE, VOLUME AND TEMPERATURE CHANGES DURING DRYING OF PRETREATED APRICOTS

TESLIME MAHMUTOĞLU[1], MEHMET PALA and MURAT ÜNAL

TÜBITAK Marmara Research Center
Food & Refrigeration Technologies Department
41470 Gebze/Kocaeli, Turkey

Accepted for Publication July 31, 1995

ABSTRACT

Simultaneous heat and mass transport in dehydration of apricots is presented. The moisture variation of apricots, pretreated with various combinations of sodium-meta-bisulphite and ethyl oleate solutions, was analyzed by Exponential and Page equations. Use of ethyl oleate in addition to sodium-meta--bisulphite as a pretreatment solution was observed to decrease drying times of apricots. The system of differential equations determining the unsteady-state temperature distribution was solved. Thermophysical properties were taken to be moisture dependent. The variation of volume upon drying (shrinkage) was introduced into the solution by taking space intervals to be variable in the apricot side while they were taken to be constants in the stone side. The dominant mass transfer mechanism was diffusion while diffusivity of water changed depending upon the pretreatment solution. Comparison between predicted and experimental data shows good agreement for both moisture and temperature variation of the apricots throughout the drying process.

INTRODUCTION

The conventional practice to dry apricots in Turkey is to treat unpitted fresh apricots with sulphur and then to expose to the sun. The fruits are partially dried from a initial moisture content of about 80% to a moisture content of 50-55%, then the fruits are pitted and let to dry to a final moisture content of about 25-28%.

---

[1] To whom correspondence should be addressed.

Journal of Food Processing and Preservation **19**(1995) 467–490. *All Rights Reserved*

In general, dehydration of apricots comprises two main operations: sulphuring the fresh fruit and drying the sulphured fruit. The sulphuring has the purpose of keeping the desired orange-to-yellow color as well as destroying microorganisms of the final dried product. However, the sulphuring agent should deeply penetrate the fruit and should be retained there as much as possible during the subsequent drying operation (Torrey 1974). With the conventional ways of sulphuring (either by combustion of sulphur or by soaking in aqueous SO_2 solutions), the penetration is too slow and time - consuming. To avoid these drawbacks, various pretreatments, such as use of alkali metal hydroxide solutions, have been suggested by several workers (Torrey 1974). Pretreatment of various foods with alkaline emulsions of ethyl oleate to increase drying rates have been investigated in literature (Bolin *et al.* 1975, Suarez *et al.* 1984, Masi and Riva 1988, Saravacos *et al.* 1988). Abdelhaq and Labuza (1987) reported a study on surface response statistical design for apricot drying, concluding sulphiting-drying using 800-1000 ppm SO_2 at any temperature in the range 50--80C to be the best treatment. However, use of ethyl oleate (AEEO) together with sodiummeta-bisulphite (SMBS) solutions to increase drying rates and to have a compatible color with sun dried fruit is not reported for apricot dehydration in literature.

Drying is a process concerning simultaneous heat and mass transfer. Heat supply can be by direct contact, by convection or by radiation (Kreyger 1972). When drying occurs by evaporation of moisture from the exposed surface of a solid, moisture must move from the depths of the solid to the surface. The mechanisms of the movement may be either by liquid diffusion or by capillary movement. In general, liquid diffusion occurs in nonporous solids, while capillary movement occurs in porous solids. During drying of many food materials, the movement of water in the falling-rate period usually occurs by diffusion (Geankoplis 1983).

Simultaneous heat and mass transport in drying foods represents a complex, irreversible process. Undesirable effects could be minimized and the process could be better controlled, if temperature and moisture distributions in foods with respect to time could be accurately predicted (Balaban and Pigott 1988). A reliable model for simulating temperature and moisture transfer in food is required to properly design drying processes (Sakai and Hayakawa 1992). Further, to carry on an optimization problem of the drying process, we must know its mathematical model and the values of its parameters. There are many references in literature concerning the kinetics of moisture distribution (Vaccarezza *et al.* 1974; Vaccarezza and Chirife 1978; Aguerre *et al.* 1985; Raouzeos and Saravacos 1986; Riva and Peri 1986; Saravacos *et al.* 1988; Masi and Riva 1988; Shepherd and Bhardwaj 1988; Tolaba and Suarez 1988; Rahman and Lamb 1991; Tolaba *et al.* 1991) and temperature ditribution (Alzamora *et al.* 1979; Kallel *et al.* 1993) occuring during drying. Most of the models available in the literature to predict temperature and moisture distribution assume shrinkage to be negligible. Most foods, such as fruits, contain a large amount of free water when they are fresh. Shrinkage, upon evaporation of this initial water, is an important characteristic. Several researchers have investigated shrinkage during food drying. Among them, Suzuki *et al.* (1976) investigated the shrinkage in dehydration of root vegetables and considered uniform, core and semicore drying models. They concluded that the uniform drying model agreed with the measured values during the early stages of the drying while the core drying model was in better agreement with their experimental results throughout the operation. Balaban and Pigott (1986) studied three dimensional shrinkage of ocean perch during drying and reported a linear relationship between the percent change in one dimension and volume fraction of water. Lozano *et al.* (1983) reported a model where the water loss-based-bulk shrinkage coefficient depended on composition of the foodstuff. Uddin *et al.* (1990) investigated a power law relation between sample thickness and moisture content during drying of pineapple. Lang and Sokhansanj (1993) considered bulk volume shrinkage of canola and wheat, and concluded that the volume decreased exponentially with time as drying proceeds. Besides shrinkage, case hardening is another phenomenon that may occur if the foodstuff is exposed to too high a temperature. Case hardening presents a barrier to moisture migration and slows the drying rate.

In this study, the variations in the volume, moisture and temperature with respect to time during dehydration of apricots, pretreated with various combinations of AEEO and SMBS solutions are presented. The transient one dimensional energy equation, with the initial and boundary conditions, was solved by converting the derivatives into finite differences concerning variable lengths of intervals with time at the apricot side, while constant lengths of intervals are assumed in the stone side.

MATERIALS AND METHODS

Mathematical Modelling

Liquid or vapor diffusion was assumed to be the primary mass transfer mechanism in the drying of apricots. The most widely investigated theoretical model in the thin layer drying of various foods is given by the solution of Fick's second law (Hutchinson and Otten 1983):

$$\frac{\delta M}{\delta t} = \nabla . (D_{eff} . \nabla M) \tag{1}$$

with the assumptions: (1) the principal driving force for mass transport is the internal moisture gradient, (2) temperature within the fruit is constant, (3) either liquid or vapor diffusion predominates (Hutchinson and Otten 1983).

Dimensions of the unpitted apricots described in experimental section, emphasized to us that apricots can be treated in spherical coordinates. The solution of Eq. 1 for constant diffusion coefficient, after making a number of simplifying assumptions and with suitable boundary conditions, for spherical coordinates (Fig. 1) gives:

$$\frac{\overline{M}-M_e}{M_i-M_e}=\frac{6}{\pi^2}\Sigma_1^\infty\frac{1}{n^2}\exp\left(-n^2\pi^2\frac{D_{eff}\,t}{R_2^2}\right) \tag{2}$$

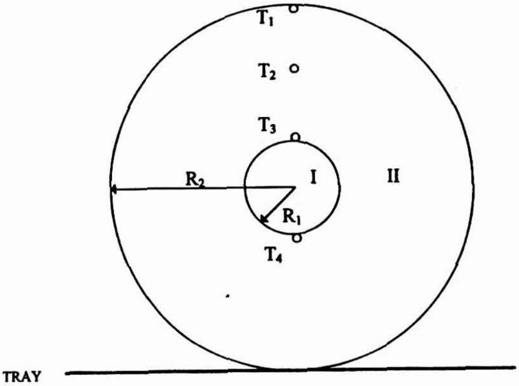


FIG. 1. SCHEMATIC REPRESENTATION OF AN APRICOT TAKEN TO BE AS A SPHERE
Region 1: Stone (Kernell + Shell), Region II, Apricot

The values of the equlibrum moisture content, M_e, are relatively small as compared to $\overline{M}$ or M_i (Alzamora *et al.* 1979), so $(\overline{M} - M_e)/(M_i - M_e)$ is simplified to $\overline{M}/M_i$. For the linear portions of log $\overline{M}/M_i$ vs t graph, Eq. 2 can be further simplified to a straight line equation:

$$\log\frac{\overline{M}}{M_i}=\log\left(\frac{6}{\pi^2}\right)-\frac{\pi^2D_{eff}\,t}{2.3\,R_2^2} \tag{3}$$

Eq. 3 can also be written in a more simplified form as:

$$\frac{\overline{M}}{M_i}=K\exp(-c\,t) \tag{4}$$

Another equation which is widely used for thin layer drying studies is the Page equation (Diamante and Munro 1993):

$$\frac{\overline{M}}{M_i} = \exp(-x\, t^{y}) \tag{5}$$

During the drying of apricots, it was observed that shrinkage occurs with a final volume reduction of about 70%. Then variation of volume with respect to moisture content of the apricots was formulated as follows (with r^2 values of about 0.96-0.99):

$$V = a + b\,M \qquad \text{for } R_2 \geq r > R_1 \tag{6}$$

Here, shrinkage was assumed to occur only in region II (Fig. 1). In other words, the volume of region I (stone side) was assumed to remain constant throughout the drying operation.

The temperature distribution for spherical coordinates is written as (Bird *et al.* 1960):

$$\frac{1}{\alpha(\overline{M})}\frac{\delta T(r,t)}{\delta t} = \frac{2}{r}\frac{\delta T(r,t)}{\delta r} + \frac{\delta^2 T(r,t)}{\delta r^2} \tag{7}$$

with the initial and boundary conditions:

$$T(r,0) = T_i \tag{8}$$

and at $r = R_2$ (surface):

$$k_{II}(\overline{M})\frac{\delta T(r,t)}{\delta r} + h\,(T_a - T_{R_2}(t) + \frac{\lambda m_s}{A(\overline{M})}\frac{\delta \overline{M}(t)}{\delta t} = \rho\, C_p \frac{V(\overline{M})}{A(\overline{M})}\frac{\delta T(r,t)}{\delta t} \tag{9}$$

where $(\overline{M})$ is the volume of half of the element next to the surface in the accumulation term. However, while the fruit shrinks, the length of an interval next to the surface and hence $(\overline{M})$ will diminish as drying proceeds, so the accumulation term in Eq. 9 was assumed to be negligible compared to other terms.

at $r = R_1$ (interface);

$$-k_I \frac{\delta T_I(r,t)}{\delta r_I} = -k_{II}(\overline{M})\frac{\delta T_{II}(r,t)}{\delta r_{II}} \tag{10}$$

and $T_I = T_{II} = T_{n*}$, at the interface (11)

at the center, $\frac{\delta T}{\delta r} = 0$ (12)

Equations 7, 9 and 10 can be written in finite difference form as:

$$\frac{1}{\alpha(\overline{M})}\frac{T_n^{t+1} - T_n^t}{\Delta t} = \frac{2}{r_n}\frac{T_{n+1}^t - T_{n-1}^t}{2\Delta r} + \frac{T_{n+1}^t + T_{n-1}^t - 2T_n^t}{\Delta r^2} \tag{13}$$

$$k_{II}(\overline{M})\frac{T_{N-1}^t - T_N^t}{\Delta r_{II}} + h\,(T_a - T_N^t) = -\left(\frac{\lambda m_s}{A(\overline{M})}\right)\left(\frac{\overline{M}^{t+1} - \overline{M}^t}{\Delta t}\right) \tag{14}$$

$$-k_I\left[\frac{3T_{n*}^{t+1} - 4T_{n*-1}^{t+1} + T_{n*-2}^{t+1}}{2\Delta r_I}\right] = -k_{II}(\overline{M})\left[\frac{-3T_{n*}^{t+1} + 4T_{n*+1}^{t+1} - T_{n*+2}^{t+1}}{2\Delta r_{II}}\right] \tag{15}$$

Equation 13 is valid for the internal nodes, where the number of nodes for region I was designated to be n* and number of nodes for region II was designated to be N. Equation 14 is for the surface node, T^{t+1}_N and the accumulation term was neglected. Equation 15 is for the interface temperature, T_{n*}, i.e. for the surface temperature of the stone. Here, while the length of an interval in region I, Δr_I, remains constant, the length of an interval in region II, Δr_{II}, is dependent on the moisture content with Eq. 6. In other words, the space between two nodes in region II shrinks as drying proceeds.

Since the explicit form of the time derivatives of the temperature was included in the equations above, stability criteria were also found by applying the second law of thermodynamics, as the coefficient of T^t_n should not be negative so that Δt should be chosen as depending on Δr (Kakac and Yener 1979).

Experimental

Apricots (var. Hacihaliloglu), growing in Malatya region of Turkey, were harvested, sorted and treated with various combinations of AEEO/SMBS solutions as shown in Table 1. They were then dried as a single layer in a batch type drier (APV & PASILAC) where air is flowing perpendicular to the fruits. The initial load density of the tray was 7.76 kg/m². Temperature of drying air was 60C and air velocity was 0.43 m/s. Weight loss of the drying apricots was measured by means of a load cell (REVERE SHB-0.05 CC) which sends signals

TABLE 1.
QUALITY PARAMETERS OF APRICOTS PRIOR TO AND AT THE END OF DRYING

		INITIAL VALUES							FINAL VALUES						
CODE	Treatment	SO_2 (ppm)	Dry Matter (g/100 g)	Water solubles (Brix)	Acidity (g/100 g)	L	+a	+b	SO_2 (ppm)	Dry Matter (g/100 g)	Water solubles (Brix)	Acidity (g/100 g)	L	+a	+b
SMAE1	SMBS[1] + ethyl oleate[2]	328.9	20	19.6	0.18	52.56	5.77	26.79	660.3	80.16	73.0	0.62	41.24	12.37	22.03
SMAE2	SMBS[1] + ethyl oleate[2]	818.0	20	22.97	0.21	43.75	4.75	21.42	3027	80.30	75.8	0.81	47.09	10.66	24.78
SMBS1	SMBS[1]	793.0	20	22.6	0.29	52.49	5.78	26.64	2059	76.11	71.9	0.79	35.30	6.83	16.95
SMBS2	SMBS[1]	2276.3	20	20.2	0.41	46.63	5.98	26.64	7019.8	81.70	75.0	1.21	43.59	10.57	23.26
AEEO	ethyl oleate[2]	-	20	19.7	0.24	56.08	6.15	27.9	-	79.08	73.8	0.79	34.30	10.35	16.15
Natural	-	-	20	18.8	0.24	63.16	7.61	31.04	-	-	-	-	-	-	-

[1] Sodium-meta-bisulphite solution: 8-15 % (Prepared to give desired initial SO_2 level of the fruit), dipping time: 20 min

[2] Ethyl oleate solution : 1.5 % Ethyl oleate + 2.0 % K_2CO_3, dipping time: 1 min.

TABLE 2.
COMPOSITION OF APRICOT[1]

Component	Apricot	Shell of stone	Kernel of stone
Moisture (g/100g)	80.00	11.90	5.0
Carbohydrates (g/100g)	18.80	82.00	24.2
Crude protein (g/100g)	0.90	1.90	19.9
Ash (g/100g)	0.08	1.70	1.42
Fat (g/100g)	0.17	2.50	49.4

[1] Vit. C (14 mg/100g) and malic acid (0.24g/100g) are also found in apricot.

to a digital indicator (ESIT) connected to a computer (Serial Port RS-232). Weight loss was measured in one minute intervals.

Average dimensions of the apricots were: (1) thickness = 3.37 cm, (2) length = 3.46 cm, (3) width = 3.31 cm. Average diameter of the stones was 1.42 cm.

Thermocouples (Cu - constantan, ± 0.1C) of diameter 1.2 mm were inserted at positions shown in Fig.1 to measure temperatures as functions of time and position. Temperature measuring system used was a microprocessor (Ellab CMC821).

The volume displacement method was used to measure volumes of the drying samples at various time intervals by means of rapeseed filled into a measure.

Other parameters measured were color (Minolta Chroma-Meter CR300; Hunterlab), SO_2 as ppm by Reith and Willams method (Turkish Standards-485, 1992), Brix (Atago Hand Refractometer), dry matter (AOAC 1984, method no. 14.125), and total acidity as malic acid (AOAC 1984, method no. 942.15).

Thermophysical Properties

Thermal conductivity and specific heat values were obtained from the following empirical relations (Sweat 1986):

$$k=0.58X_w+0.155X_p+0.25X_c+0.16X_f+0.135X_a \text{ (W/m K)} \tag{16}$$

$$Cp = 4.18\ X_w + 1.711\ X_p + 1.928\ X_f + 1.547\ Xc + 0.908\ X_a \text{ (kJ/kg K)} \tag{17}$$

where X_w X_p, X_c, X_f and X_a are the mass fractions of the water, protein, carbohydrate, fat and ash components of the food in question (the components of apricot are given in Table 2, where methods are described by Canellas *et al.* 1992, and Tuncel *et al.* 1990). In our model, the initial amounts of the constituents other than water were assumed to remain constant throughout the drying process, hence k and Cp values of the region II were related to the average moisture content (M) at any time of drying from:

$$M_T(t) = (\overline{M}(t)\,m_s) + m_s \tag{18}$$

$$X_i(t) = \frac{Initial\ Value}{M_T(t)}, \qquad \text{where } i = p, c, f \text{ or } a. \tag{19}$$

$$X_w(t) = \frac{\overline{M}(t)\,m_s}{M_T(t)} \tag{20}$$

The densities were calculated from the measured mass to volume ratio. Convective heat transfer coefficient was determined from the temperature histories of the samples by comparing with predicted values: the sums of squares of differences between the experimental and predicted data were minimized by a gradient method (Sakai and Hayakawa 1992; Ozilgen and Heil 1994).

Method of Solution

The Exponential (4) and Page (5) equations were tested for the experimental $\overline{M}$ vs t data. The one giving the highest r^2 was chosen to represent variation of M with respect to t, and inserted into Eq. 14. Similarly, variation of the volume with respect to moisture content was found for each run in the form of Eq. 6 and inserted into eqs. 13, 14 and 15 in combination with Eqs. 16 and 17.

Shrinkage was assumed to be equal in all dimensions of the sphere. Number of nodes both in the region I and in the region II was taken to be constants. But the length of intervals in the region II was assumed to decline as the fruit shrinks, while those in the region I were assumed to remain constant. Temperature distribution as a function of radius and time was then found by writing a BASIC program. The program stopped when the experimental pitting time of the fruits was achieved.

RESULTS AND DISCUSSION

Effects of the initial treatments on the final dried product can be summarized as follows: a/b (redness/yellowness) ratio of the natural-fresh apricot, 0.245, changed to the values of 0.215, 0.221, 0.216, 0.224 and 0.220 for the runs SMAE1 to AEEO (with the order as reported in Table 1) after pretreatment, and further to 0.560, 0.430, 0.402, 0.454 and 0.640, respectively, after the drying operation. It is seen that, pretreatment solutions decreases L and a/b values just prior to drying. However, at the end of drying, a relative rise in the a/b ratio is seen, especially in the AEEO treated products alone, indicating that AEEO has no detrimental effect on the browning reactions,which are the main source of the unwanted dark color. In other words, the quality of the final product seems to be affected by both the residual concentration of the SO_2 and the presence of AEEO: the first one causes final product to have a desired color while the second one increses the drying rates, as will be discussed below. It may be claimed that, in terms of apparent quality factors of the final product, AEEO treated products should be rejected while (AEEO+SMBS) treated but with a lower residual concentration should be suggested.

Usually the drying rate curves show a tendency to have a constant rate period followed by the falling rate period. However, for the dehydration of apricots we did not observe a constant rate period which would otherwise cause nonuniformity in the moisture content of the fruit. In order to emphasize this observation Biot number was found from (Saravacos *et al.* 1988):

$$Bi = \frac{k_m (D_e / 2)}{D_{eff}} \tag{21}$$

where k_m is the mass transfer coefficient at the surface and obtained from (Saravacos *et al.* 1988):

$$Sh = \frac{k_m D_e}{D_{AB}} = 2 + 0.6\,\mathrm{Re}^{0.5}\, Sc^{0.33} \tag{22}$$

By inserting drying conditions employed in our experiments, k_m was found to be about 0.011 m/s. Hence Biot numbers, depending on the observed D_{eff} for each run studied was found to be very large. Then it was concluded that, mass evaporation from the surface (external resistance) is not important and diffusional mechanism (internal resistance) gives the primary resistance to mass transfer.

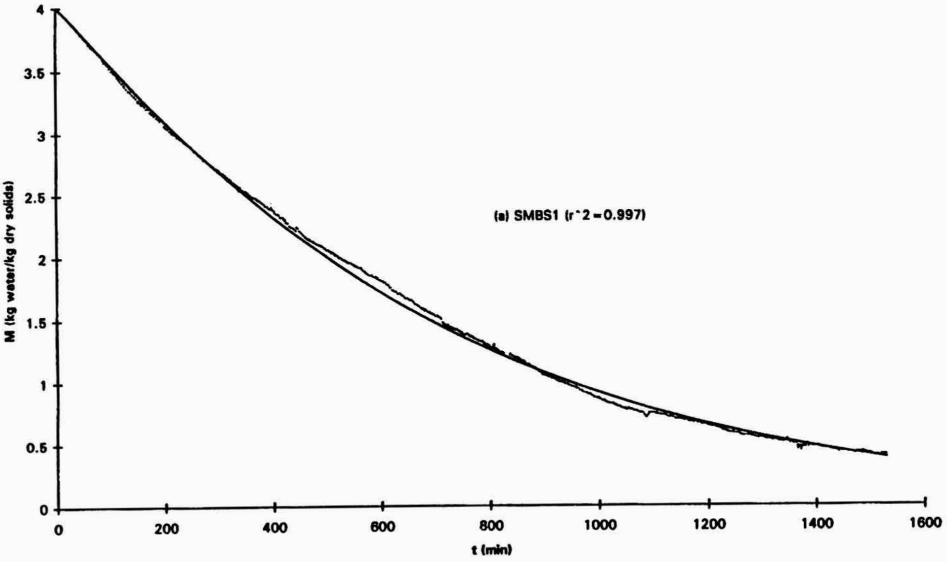
TABLE 3.
PARAMETERS OF THE MODEL EQUATIONS TO PREDICT MOISTURE AND VOLUME CHANGES

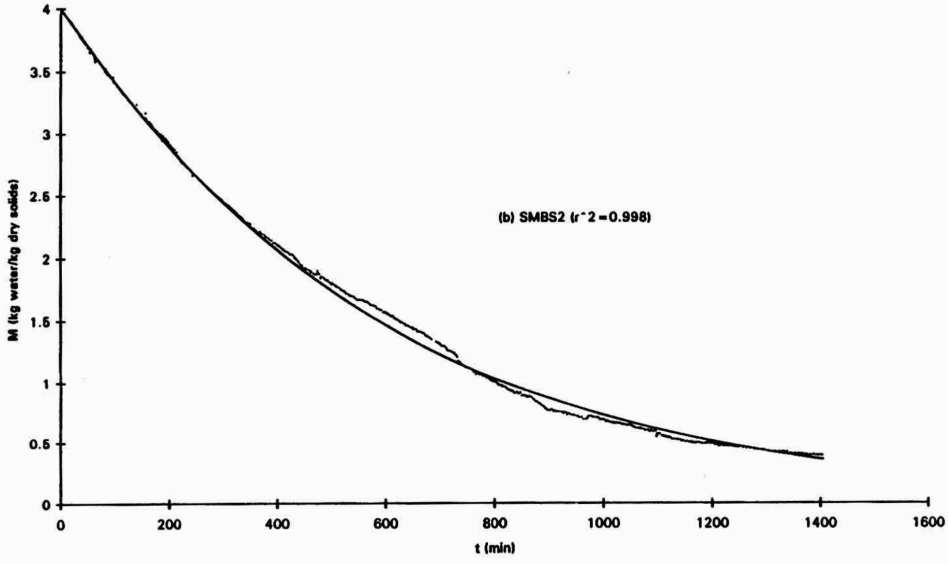
CODE	x	y	a	b
SMAE1	1.146×10^{-3}	1.085678	4.55	4.55
SMAE2	1.121×10^{-3}	1.092599	5.14	5.26
SMBS1	7.814×10^{-3}	1.092549	5.97	4.89
SMBS2	1.357×10^{-3}	1.032637	5.30	4.24
AEEO	1.360×10^{-3}	1.080321	4.70	4.28

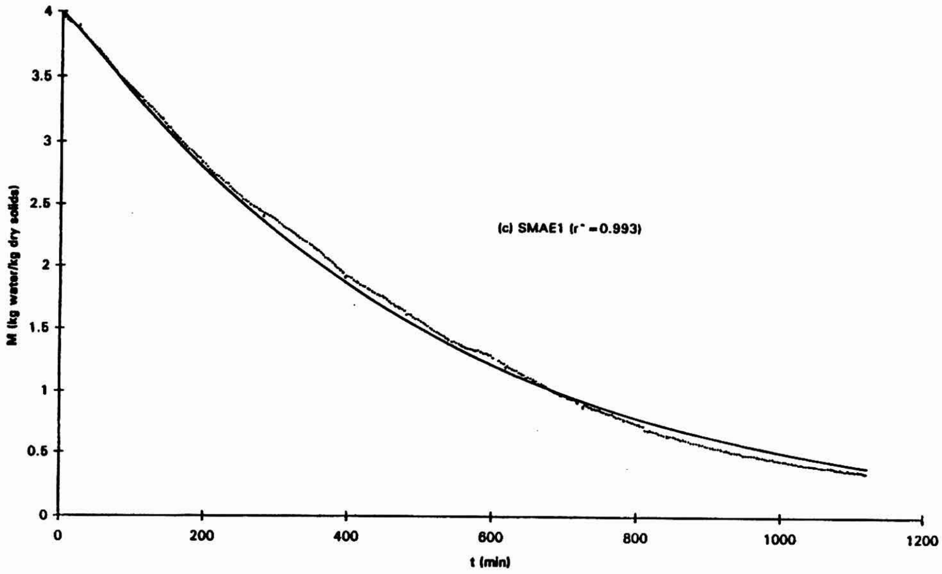
$M/M_i = exp\,(-x\,t^y)$

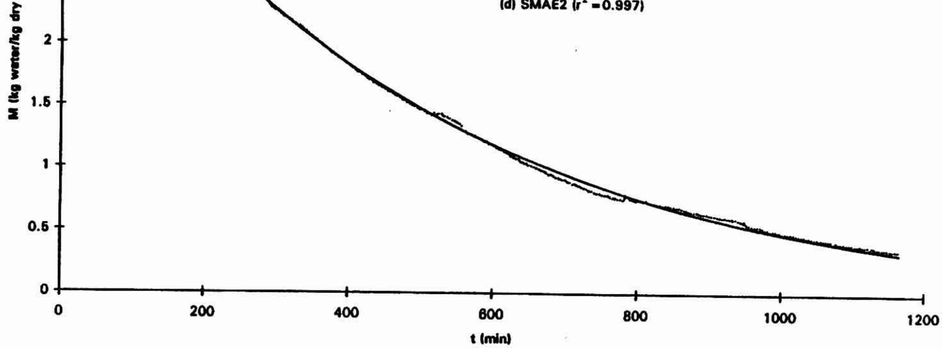
$V = a + b\,M$

When experimental $\bar{M}$ vs t data are analyzed for the Exponential and Page equation the difference between r^2-values of those equations was small for all runs. However, Page Equation gave slightly higher r^2-values (Table 3). The variations of moisture content with respect to time are given in Fig. 2a-e, for the runs studied. The model predictions and the experimental results are in good agreement. To calculate D_{eff}, semi-log plots of M/M_i vs t were performed for each run (an example is given in Fig. 3 for SMAE1). D_{eff} was calculated from the slopes of log (M/M_i) vs t graphs (Lomauro *et al.* 1985). It was observed that there is a linear relationship but the slopes are changing at some break points. This observation indicates that, D_{eff} is changing at some moisture contents. The results calculated for each linear portion of log $\bar{M}/M_i$ vs t graphs are reported in Table 4, where overall D_{eff} values are also reported. By comparing with $\bar{M}$ vs t graphs (Fig. 2a-e), it was seen that, the first break point usually corresponds to the pitting time of the fruit. In other words, the presence of the stones decreases the drying rates of the whole apricots. Based on these results, it is possible to conclude that, there is a slight increase in the D_{eff} values of each run after pitting. However, at the second break point D_{eff} values again decreases due


4
3.5
3
2.5
2
1.5
1
0.5
0
M (kg water/kg dry solids)
(a) SMBS1 (r^2=0.997)
0
200
400
600
800
1000
1200
1400
1600
t (min)


4
3.5
3
2.5
2
1.5
1
0.5
0
M (kg water/kg dry solids)
(b) SMBS2 (r^2=0.998)
0
200
400
600
800
1000
1200
1400
1600
t (min)


(c) SMAE1 (r^ =0.993)
M (kg water/kg dry solids)
4
3.5
3
2.5
2
1.5
1
0.5
0
0
200
400
600
800
1000
1200
t (min)


(d) SMAE2 (r^ =0.997)
M (kg water/kg dry solids)
4
3.5
3
2.5
2
1.5
1
0.5
0
0
200
400
600
800
1000
1200
t (min)

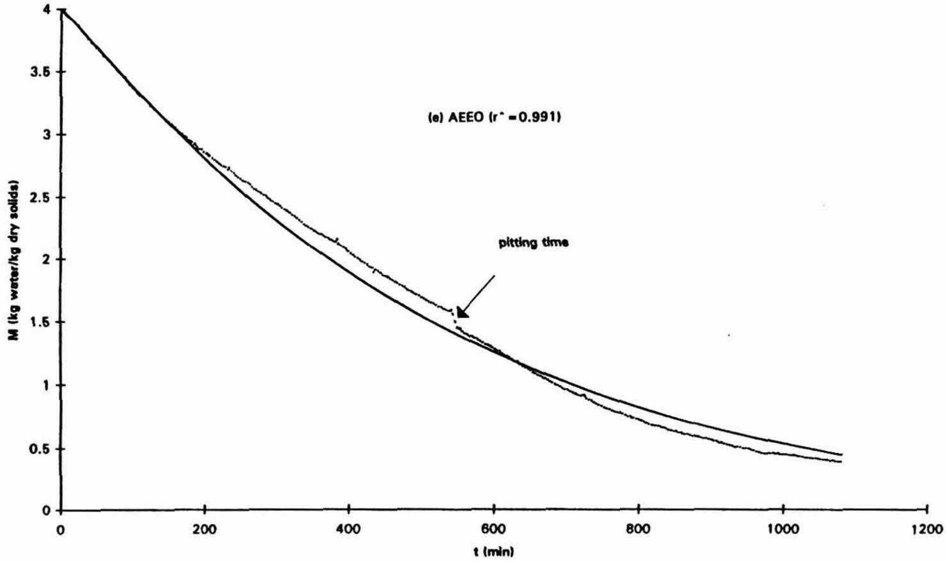


FIG. 2. COMPARISON OF THE PREDICTED (___) AND EXPERIMENTAL (---) MOISTURE CONTENTS

to decreasing moisture content. In agreement with the fact that ethyl oleate not only removes the waxy layer surrounding the skin but also diffuses into the fruit, thus improving external and internal water transport (Aguilera *et al.* 1987), ethyl oleate treated products had the highest overall diffusion coefficient compared to the SMBS treated products. The drying rates of different treatments can be classified as: SMAE2 > SMAEl > AEEO > SMBS2 > SMBS1. However, at the end of drying, the difference between the drying rates of SMAE2, SMAE1 and AEEO diminishes. Ethyl oleate breaks the surface resistance to mass transfer and increases the diffusion coefficients as confirmed by the results reported in Table 4.

In order to check the hypothesis that temperature distribution with respect to position diminishes after a short time at the beginning, figures similar to Fig. 4 (for AEEO) were plotted for all runs. Although a small temperature gradient exists at the very beginning of the runs, it was then negligible. Consequently, average temperature was thought to represent variation of temperature with respect to time and position:

$$\overline{T}=\frac{\iint_{A} T dA}{A} \tag{23}$$

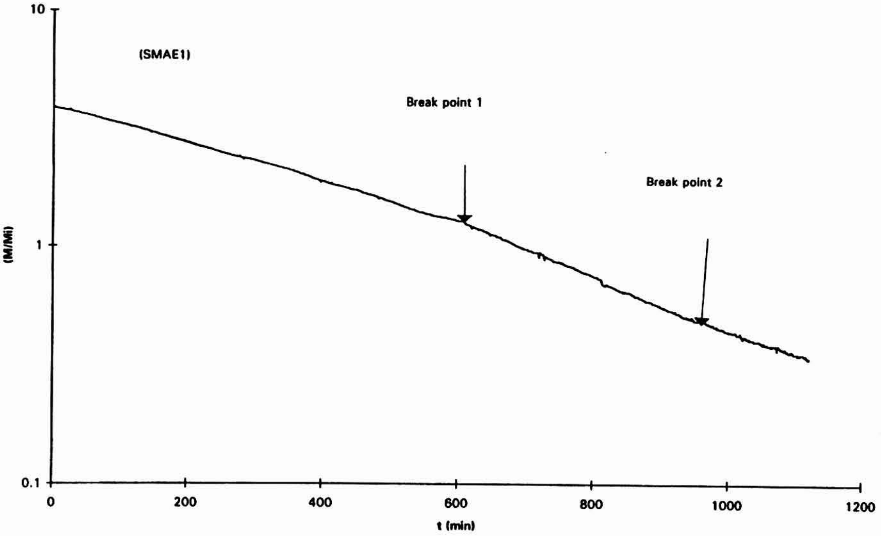


FIG. 3. SEMI-LOG PLOT OF M/M_i vs t, FOR SMAE1
Break points show the moisture contents where the diffusivity (D_{eff}) changes.

TABLE 4.
STEPWISE AND OVERALL CHANGE OF DIFFUSION COEFFICIENT FOR DIFFERENT TREATMENTS

CODE	Pitting Time (min.)	D_{eff} (m^2/s)	$\overline{M}$ (kg water / kg dry solids)	Overall D_{eff} (m^2/s)
SMBS1	825	7.40×10^{-10}	4.000 - 1.493	8.90×10^{-10}
		1.10×10^{-09}	1.493 - 0.714	
		8.40×10^{-10}	0.714 - 0.400	
SMBS2	686	7.70×10^{-10}	4.000 - 1.417	9.00×10^{-10}
		1.20×10^{-09}	1.417 - 0.768	
		7.10×10^{-10}	0.768 - 0.387	
SMAE1	601	9.40×10^{-10}	4.000 - 1.286	1.15×10^{-09}
		1.31×10^{-09}	1.286 - 0.389	
		9.77×10^{-10}	0.389 - 0.335	
SMAE2	557	1.10×10^{-09}	4.000 - 1.234	1.22×10^{-09}
		1.40×10^{-09}	1.234 - 0.749	
		9.40×10^{-10}	0.749 - 0.553	
		1.30×10^{-09}	0.553 - 0.351	
AEEO	542	9.40×10^{-10}	4.000 - 1.450	1.30×10^{-09}
		1.50×10^{-09}	1.450 - 0.477	
		8.70×10^{-10}	0.477 - 0.386	

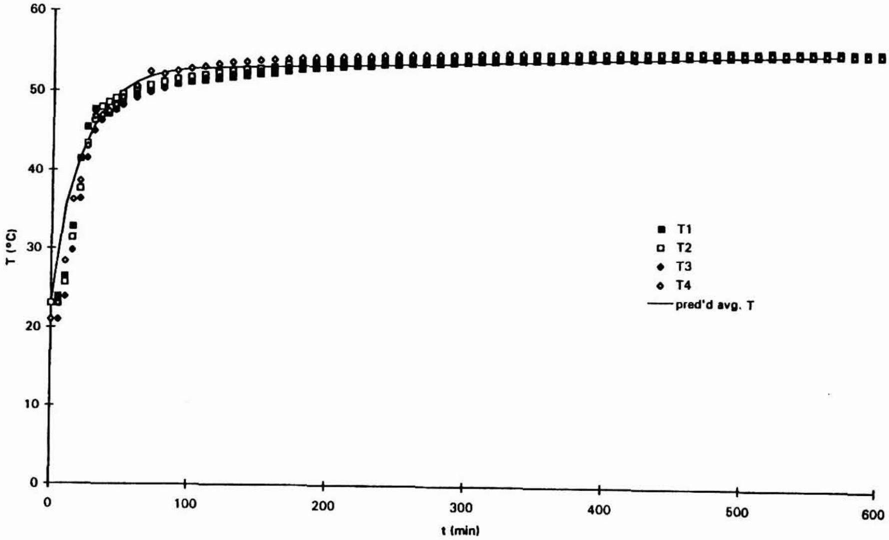


FIG. 4. VARIATION OF TEMPERATURE WITH RESPECT TO TIME AND POSITION, FOR AEEO

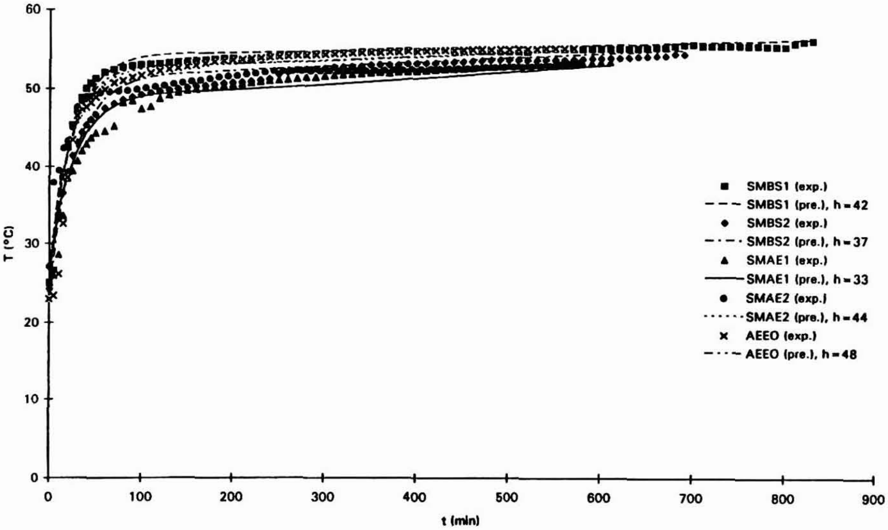


FIG. 5. COMPARISON OF PREDICTED AND EXPERIMENTAL AVERAGE TEMPERATURES FOR DIFFERENT PRETREATMENTS
Units of h is W/(m^{2}K).

The results of the predicted and experimental average temperatures are given in Fig. 5. It is interesting that, the rates of initial rise of temperatures are different for the runs studied: SMBS1 > AEEO > SMAE2 > SMBS2 > SMAE1. It should be noted that this classification is not the same as the one given for the drying rate. However, with some exceptions, it may be claimed that the one having the highest temperature rise at the beginning has the lowest drying rate. A reason for this may be the well known case hardening, which prevents migration of water from the surface through the air.

In order to see the effects of surface characteristics of a particular pretreatment on the temperature rise of the product, number of ridges per unit area were observed by a zoom stereomicroscope (WILD Heerbrugg) with a magnification of 6.0. For the final dried products, qualitatively the classification was: SMAE2 < SMAE1 < SMBS2 < AEEO < SMBS1, in terms of the number of ridged surface per unit area. Additionally, on the surface of SMBS1 case hardening was observed. It is seen that, as the ridgedness of the surface increases, initial rise of temperature increases. An explanation for this may be that the ridged surfaces act as fins (extended surfaces), thus increasing convective heat transfer coefficients and hence heat transfer rates.

The convective heat transfer coefficient between the fruit surface area and the air is mainly influenced by the heat flux, surface area and the temperature difference:

$$h = \frac{q}{(A)(\Delta T)} \tag{24}$$

We have tried several empirical correlations, such as Eq. 25 and 26 to find h (Geankoplis 1983):

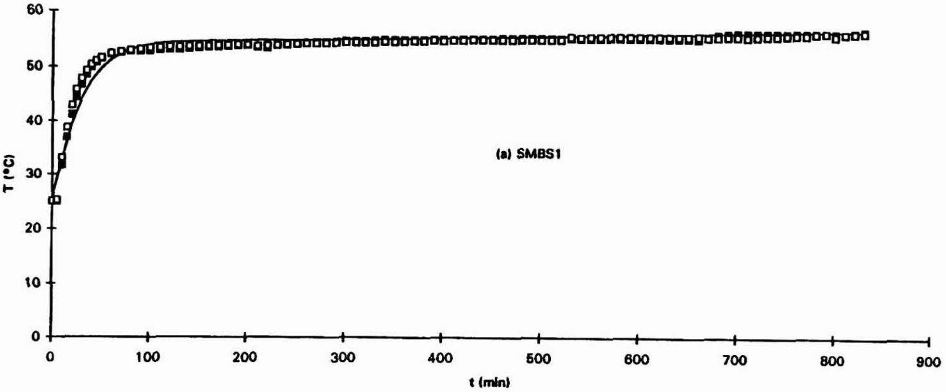
for cross flow, $h = 1.17G^{0.37}$ (W/m^2.K) (25)

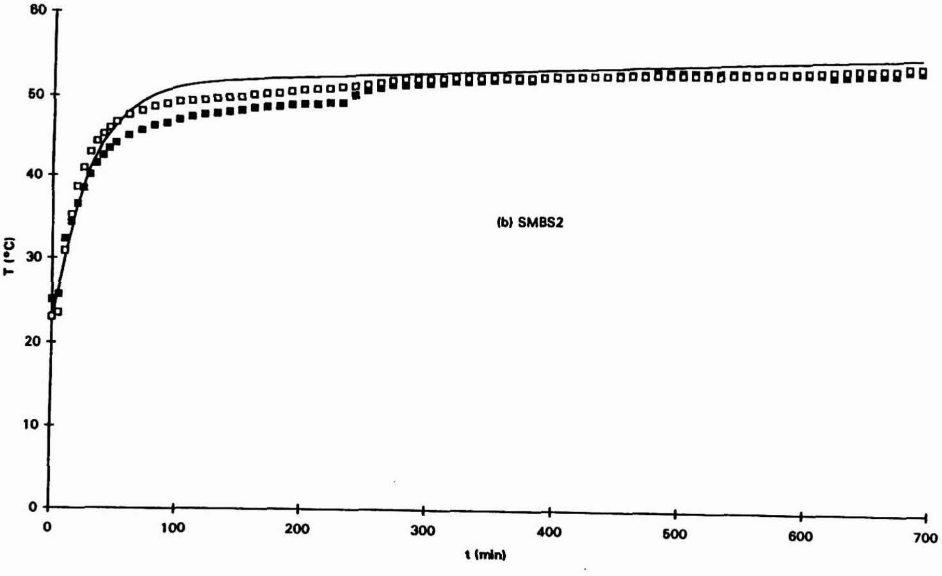
where $G = v.p$ (kg/m^2.h)

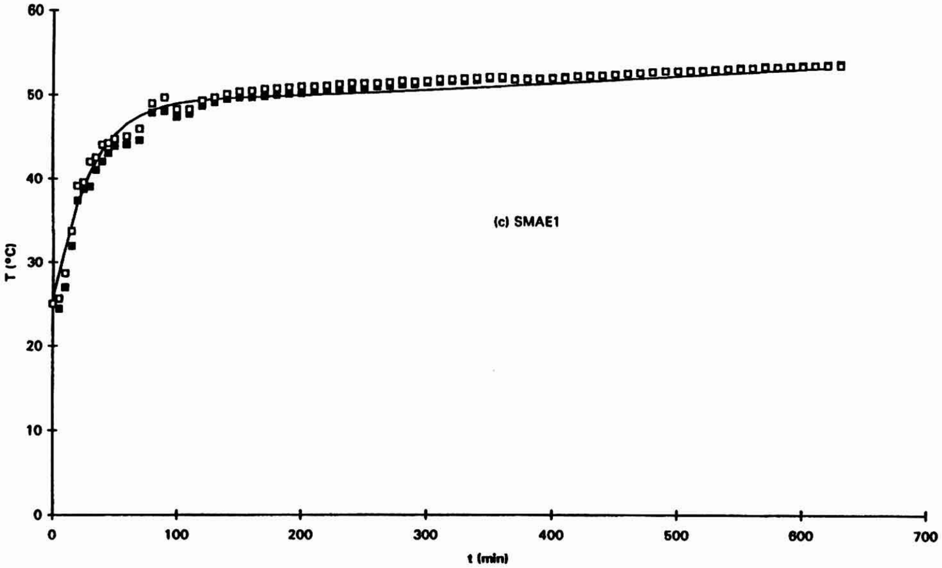
and for heat transfer of gases in beds of spheres,

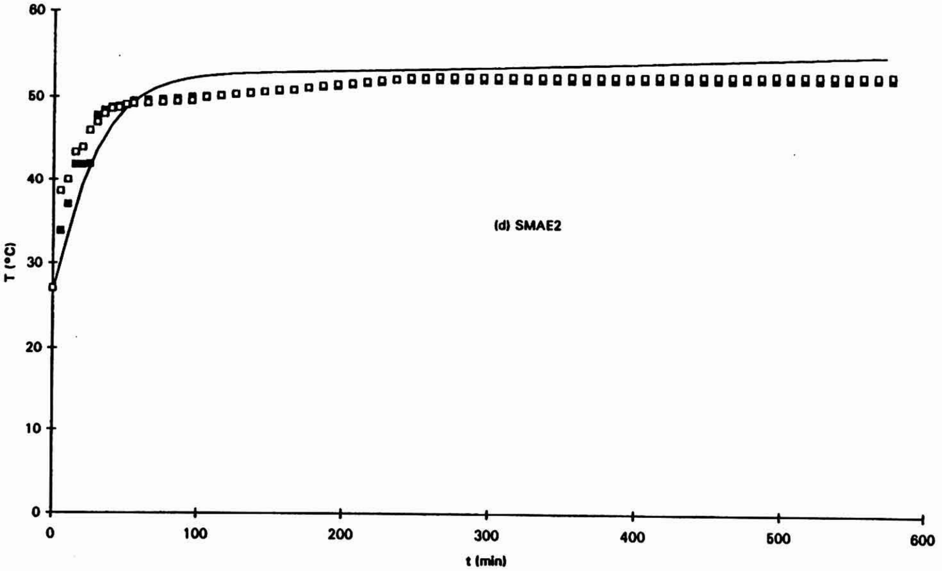
$$\varepsilon \frac{h}{Cp\,v'\,\rho}\left(\frac{Cp\,\mu}{k}\right)_f^{2/3} = \frac{2.876}{\mathrm{Re}} + \frac{0.3023}{\mathrm{Re}^{0.35}} \tag{26}$$

The values of h's obtained from Eq. 25 or 26 were about 18-22 W/m^2.K, giving predicted temperatures to be lower than the experimental ones. Then, h values


(a) SMBS1
T (°C)
t (min)
0
10
20
30
40
50
60
0
100
200
300
400
500
600
700
800
900


(b) SMBS2
T (°C)
t (min)
0
10
20
30
40
50
60
0
100
200
300
400
500
600
700


60
50
40
30
20
10
0
T (°C)
0
100
200
300
400
500
600
700
t (min)
(c) SMAE1


60
50
40
30
20
10
0
T (°C)
0
100
200
300
400
500
600
t (min)
(d) SMAE2

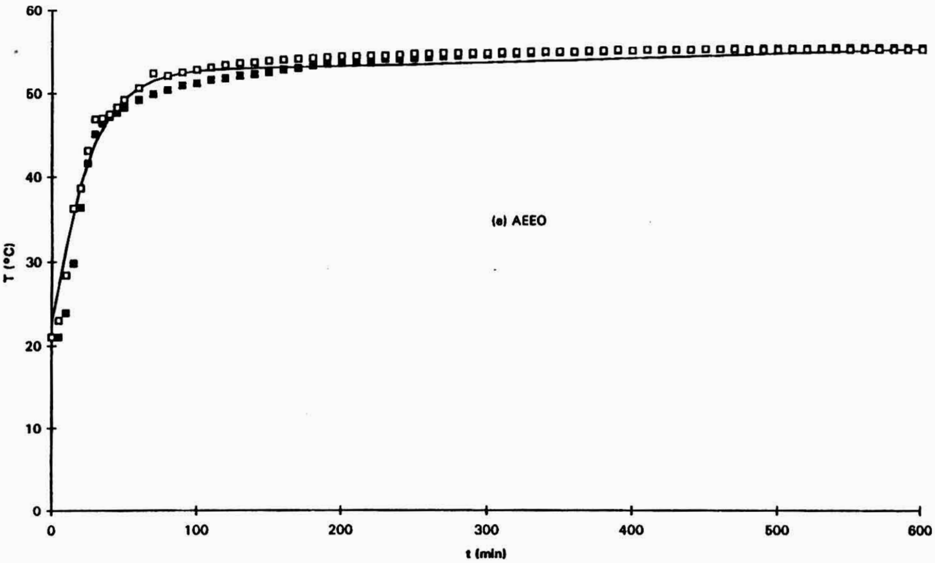


FIG. 6. COMPARISON OF PREDICTED AND EXPERIMENTAL STONE SURFACE TEMPERATURES: (■) T3; (□) T4; (___) PREDICTED T_{n*}.

giving the least sums of squares of differences between the predicted and experimental results were found for each run, by a gradient procedure. The results confirmed that, those heat transfer coefficients are about 2 to 3 times as much as the ones estimated from Eq. 25 or 26. Further, it is seen that for each run a different h value is estimated (Fig. 5). However, it was observed that neither drying rate, nor surface characteristics nor percent reduction in volume has the dominant effect on the estimated h value.

Predicted stone surface temperature (T_{n*}) and experimental stone top and bottom surface (T3 and T4 in Fig. 1) temperatures are given in Fig. 6a-e. In general, the agreement of predicted and experimental results are good. However, for the runs SMBS2 and SMAE2 experimental results gets lower than the predicted ones after the temperature rising period. A reason for this may be the decrease of actual h. These confirm to the fact that, the heat transfer coefficient may be constant only within the period of a constant rate of drying, while in the falling rate period it diminishes with decreasing moisture content (Kuts and Pikus 1980). Another observation from Fig. 6a-e is that stone bottom temperature (T4) is always higher than the stone top temperature (T3) due to the conducted heat from the tray. It means the assumption of uniform temperature for a particular radius is not always true.

CONCLUSIONS

Use of ethyl oleate in addition to sodium-meta-bisulphite as pretreatment solutions for the drying of apricots cause L and a/b values to increase. Ethyl oleate and ethyl oleate plus sodium-meta-bisulphite treated apricots have higher drying rates (hence lower drying times) compared to sodium-meta-bisulphite treated products alone. Drying rates, percent shrinkage and surface characteristics seem to affect the rate of temperature rise and estimated heat transfer coefficients, but the interdependence of those factors is not clear.

ACKNOWLEDGMENTS

The authors appreciate the technical assistance given by Selahattin Nas, Ibrahim Doymaz and Erkan Kirat.

NOMENCLATURE

a	Intercept (Eq.6)
A	Surface area (m^2)
b	Slope (Eq. 6)
Bi	Biot number, $k_m R/D_{eff}$
Cp	Specific heat (J/kg K)
D_{AB}	Diffusivity of water in air (m^2/s)
D_{eff}	Diffusion coefficient (m^2/s)
D_e	Equivalent diameter of sphere, $(6V/\pi)^{1/3}$, (m)
h	Convective heat trasfer coefficient (W/m^2 K)
k	Conductivity; k ($\bar{M}$): as a function of moisture content. (W/ m K)
k_m	Surface mass transfer coefficient (m/s)
K	Constant (Eq. 4)
m_s	Dry mass of solids (kg)
$\bar{M}$	Average moisture content; $\bar{M}$(t): as a function of time, (kg/kg dry solids)
M_e	Equilibrum moisture content (kg/kg dry solids)
M_i	Initial moisture content (kg/kg dry solids)
M_T	Total mass at any time (kg)
q	Heat flux (W/m^2)
r	Radius (m)
R_1	Radius of stone (m)
R_2	Radius of whole apricot (m)

Re	Reynolds number $(D_e v\rho/\mu)$
r_n	Length of a specified node (m)
Δr	Space increment (m)
Sc	Schmidt number, $(\mu/\rho D_{AB})$
Sh	Sherwood number, $(k_m D_e/D_{AB})$
t	Time (s)
$T(r,t)$	Temperature as a function of position and time (C)
T_i	Initial temperature (C)
T_I	Temperature at the stone side (C)
T_a	Air temperature (C)
T_{II}	Temperature at the apricot side (C)
T_{n^*}	Temperature at the interface (C)
Δt	Time increment (s)
v	Velocity (m/s)
$V(\bar{M})$	Volume as a function of moisture content (m^3)
x	Constant (Eq. 5)
X	Mass fraction; X_a: ash, X_c: carbohydrates, X_f: fats, X_p: proteins, X_w: water
y	Constant (Eq. 5)
α	Thermal diffusivity; $\alpha(\bar{M})$ as a function of moisture content, $(k/\rho\ Cp)$, (m^2/s)
ϵ	Void fraction
λ	Latent heat of vaporization (J/kg)
μ	Viscosity (kg/m s)
ρ	Density (kg/m^3)

REFERENCES

ABDELHAQ, E.H. and LABUZA, T.P. 1987. Air drying characteristics of apricots. J. Food Sci. *52*, 342-345.

AGUERRE, R.J., GABITTO, J.F. and CHIRIFE, J. 1985. Utulization of Fick's second law for the evaluation of diffusion coefficients in food processes controlled by internal diffusion. J. Food. Technol. *20*, 623–629.

AGUILERA, J.M., OPPERMANN, K. and SANCHEZ, F. 1987. Kinetics of browning of sultana grapes. J. Food Sci. *52*, 990-993.

ALZAMORA, S.M., CHIRIFE, J. and VOILLAZ, P. 1979. A simplified model for predicting the temperatures of foods during air dehydration. J. Food. Technol. *14*, 369-380.

AOAC 1984. *Official Methods of Analysis*, 14th ed. Association of Official Analytical Chemists, Washington, DC.

BALABAN, M. and PIGOTT, G.M. 1986. Shrinkage in fish muscle during drying. J. Food Sci. *51*, 510-511.

BALABAN, M. and PIGOTT, G.M. 1988. Mathematical model of simultaneous heat and mass transfer in food with dimensional changes and variable transport properties. J. Food. Sci. *53*, 935-939.

BIRD, R.B., STEWART, W.E. and LIGHTFOOT, E.N. 1960. *Transport Phenomena*. pp. 316-317, John Wiley & Sons, New York.

BOLIN, H.R., PETRUCCI, V. and FULLER, G. 1975. Characteristics of mechanically harvested raisins produced by dehydration and by field drying. J. Food Sci. *40*, 1036-1038.

CANELLAS, J., FEMENIA, A., ROSSELLO, Ç. and SOLER, L. 1992. Chemical composition of the shell of apricot seeds. J. Sci. Food Agric. *59*, 269-271.

DIAMANTE, L.M. and MUNRO, P.A. 1993. Mathematical modelling of the thin layer solar drying of sweet potato slices. Solar Energy. *51*, 271-276.

GEANKOPLIS, C.J. 1983. *Transport Processes and Unit Operations*. pp. 244, 524-533. Allyn and Bacon, USA.

HUTCHINSON, D. and OTTEN, L. 1983. Thin layer air drying of soybeans and white beans. J. Food. Technol. *18*, 507-522.

KAKAC, S. and YENER, Y. 1979. *Heat Conduction*. pp. 379-383, Kelaynak Publ. and Print. Co., Ankara, Turkey.

KALLEL, F., GALANIS, N., PERRIN, B. and JAVELAS, R. 1993. Effects of moisture on temperature during drying of consolidated porous materials. Trans. ASME. *115*, 724–733.

KREYGER, J. 1972. *Drying and Storing Grains, Seeds and Pulses in Temperature Climates*. pp. 41-44. IBVL, Holland.

KUTS, P.S. and PIKUS, I.F. 1980. Interdependence between heat and mass transfer in drying. In *Proceedings of the Second International Symposium - Drying 80*, Vol. 2, (A.S. Mujumdar, ed.) pp. 65-79, Hemisphere Publ. Corp. USA.

LANG, W. and SOKHANSANJ, S. 1993. Bulk volume shrinkage during drying of wheat and canola. J. Food Process Engineering *16*, 305-314.

LOMAURO, C.J., BAKSHI, A.S. and LABUZA, T.P. 1985. Moisture transfer properties of dry and semimoist foods. J. Food Sci. *50*, 397-400.

LOZANO, J.E., ROTSTEIN, E. and URBICAIN, M.J. 1983. Shrinkage, porosity and bulk density of foodstuffs at changing moisture contents. J. Food Sci. *48*, 1497-1553.

MASI, P. and RIVA, M. 1988. Modeling grape drying kinetics. In Preconcentration and Drying of Food Materials (S. Bruin, ed.). pp. 203-209, Elsevier Sci. Publ. B. V. Amsterdam.

OZILGEN, M. and HEIL, J.R. 1994. Mathematical modeling of transient heat and mass transport in a baking biscuit. J. Food Proc. Pres. *18*, 134-148.

RAHMAN, MD.S. and LAMB, J. 1991. Air drying behavior of fresh and osmotically dehydrated pineapple. J. Food Process Engineering *14*, 163-171.

RAOUZEOS, G.S. and SARAVACOS, G.D. 1986. Solar drying of raisins. Drying Technol. *4*, 633-649.

RIVA, M. and PERI, C. 1986. Kinetics of sun and air drying of different varieties of seedless grapes. J. Food. Technol. *21*, 199-208.

SAKAI, N. and HAYAKAWA, K. 1992. Two dimensional simultaneous heat and moisture transfer in composite food. J. Food Sci. *57*, 475-480.

SARAVACOS, G.D., MAROUSIS, S.N. and RAOUZEOS, G.S. 1988. Effect of ethyl oleate on the rate of air-drying of foods. J. Food Eng. *7*, 263-270.

SHEPHERD, M. and BHARDWAJ, R.K. 1988. Thin layer drying of pigeon pea. J. Food Sci. *53*, 1813-1817.

SUAREZ, C., LONCIN, M. and CHIRIFE, J. 1984. A preliminary study on the effect of ethyloleate dipping treatment on drying rate of grain corn. J. Food Sci. *49*, 236-238.

SUZUKI, K., KUBOTA, K., HASEGAWA, T. and HOSAKA, M. 1976. Shrinkage in dehydration of root vegetables. J. Food Sci. *41*, 1189-1193.

SWEAT, V.E. 1986. Thermal properties of foods. In *Engineering Properties of Foods*. (M.A. Rao and S.S.H. Rizvi, eds.) pp. 49-87, Marcel Dekker, New York.

TOLABA, M.P. and SUAREZ, C. 1988. Simulation of the thin - layer drying of corn by means of the diffusional model. Lebensm.-Wiss. u.-Technol. *21*, 83-86.

TOLABA, M.P., SUAREZ, C. and VIOLLAZ, P.E. 1991. Diffusion coefficient estimation for shelled corn. Lebensm.-Wiss. u.-Technol. *24*, 303-306.

TORREY, M. 1974. *Dehydrafion of Fruits and Vegetables*. pp. 110-143. Food Technol. Rev. No. 13, Noyes Data Corp., USA.

TUNCEL, G., NOUT, M.J.R., BRIMER, L. and GOKTAN, D. 1990. Toxicological, nutritional and microbiological evaluation of tempe fermentation with *Rhizopus oligosphorous* of bitter and sweet apricot seeds. Int. J. Food Microbiol. *13*, 337-339.

UDDIN, M.S., HAWLADER, M.N.A. and RAHMAN, MD.S. 1990. Evaluation of drying characteristics of pineapple in the production of pineapple powder. J. Food Processing Preservation *14*, 375-391.

VACCAREZZA, L.M. and CHIRIFE, J. 1978. On the application of Fick's law for the kinetic analysis of air drying of foods. J. Food Sci. *43*, 236–238.

VACCAREZZA, L.M., LOMBARDI, J.L. and CHIRIFE, J. 1974. Kinetics of moisture movement during air drying of sugar beet root. J. Food. Technol. *9*, 317-327.

AUTHOR INDEX

Journal of Food Processing and Preservation **19** (1995) 491–494. *All Rights Reserved.*

SUBJECT INDEX

FNP

PUBLICATIONS IN FOOD SCIENCE AND NUTRITION

Journals

JOURNAL OF FOOD LIPIDS, F. Shahidi
JOURNAL OF RAPID METHODS AND AUTOMATION IN MICROBIOLOGY, D.Y.C. Fung and M.C. Goldschmidt
JOURNAL OF MUSCLE FOODS, N.G. Marriott, G.J. Flick, Jr. and J.R. Claus
JOURNAL OF SENSORY STUDIES, M.C. Gacula, Jr.
JOURNAL OF FOODSERVICE SYSTEMS, C.A. Sawyer
JOURNAL OF FOOD BIOCHEMISTRY, J.R. Whitaker, N.F. Haard and H. Swaisgood
JOURNAL OF FOOD PROCESS ENGINEERING, D.R. Heldman and R.P. Singh
JOURNAL OF FOOD PROCESSING AND PRESERVATION, D.B. Lund
JOURNAL OF FOOD QUALITY, J.J. Powers
JOURNAL OF FOOD SAFETY, T.J. Montville
JOURNAL OF TEXTURE STUDIES, M.C. Bourne and M.A. Rao

Books

OF MICROBES AND MOLECULES: FOOD TECHNOLOGY AT M.I.T., S.A. Goldblith
MEAT PRESERVATION: PREVENTING LOSSES AND ASSURING SAFETY, R.G. Cassens
S.C. PRESCOTT, M.I.T. DEAN AND PIONEER FOOD TECHNOLOGIST, S.A. Goldblith
FOOD CONCEPTS AND PRODUCTS: JUST-IN-TIME DEVELOPMENT, H.R. Moskowitz
MICROWAVE FOODS: NEW PRODUCT DEVELOPMENT, R.V. Decareau
DESIGN AND ANALYSIS OF SENSORY OPTIMIZATION, M.C. Gacula, Jr.
NUTRIENT ADDITIONS TO FOOD, J.C. Bauernfeind and P.A. Lachance
NITRITE-CURED MEAT, R.G. Cassens
POTENTIAL FOR NUTRITIONAL MODULATION OF AGING, D.K. Ingram *et al.*
CONTROLLED/MODIFIED ATMOSPHERE/VACUUM PACKAGING OF FOODS, A.L. Brody
NUTRITIONAL STATUS ASSESSMENT OF THE INDIVIDUAL, G.E. Livingston
QUALITY ASSURANCE OF FOODS, J.E. Stauffer
THE SCIENCE OF MEAT AND MEAT PRODUCTS, 3RD ED., J.F. Price and B.S. Schweigert
HANDBOOK OF FOOD COLORANT PATENTS, F.J. Francis
ROLE OF CHEMISTRY IN PROCESSED FOODS, O.R. Fennema, *et al.*
NEW DIRECTIONS FOR PRODUCT TESTING OF FOODS, H.R. Moskowitz
PRODUCT TESTING AND SENSORY EVALUATION OF FOODS, H.R. Moskowitz
ENVIRONMENTAL ASPECTS OF CANCER: ROLE OF FOODS, E.L. Wynder *et al.*
FOOD PRODUCT DEVELOPMENT AND DIETARY GUIDELINES, G.E. Livingston, R.J. Moshy, and C.M. Chang
SHELF-LIFE DATING OF FOODS, T.P. Labuza
ANTINUTRIENTS AND NATURAL TOXICANTS IN FOOD, R.L. Ory
UTILIZATION OF PROTEIN RESOURCES, D.W. Stanley *et al.*
VITAMIN B_6: METABOLISM AND ROLE IN GROWTH, G.P. Tryfiates
POSTHARVEST BIOLOGY AND BIOTECHNOLOGY, H.O. Hultin and M. Milner

Newsletters

MICROWAVES AND FOOD, R.V. Decareau
FOOD INDUSTRY REPORT, G.C. Melson
FOOD, NUTRITION AND HEALTH, P.A. Lachance and M.C. Fisher
FOOD PACKAGING AND LABELING, S. Sacharow

GUIDE FOR AUTHORS

Typewritten manuscripts in triplicate should be submitted to the editorial office. The typing should be double-spaced throughout with one-inch margins on all sides.

Page one should contain: the title, which should be concise and informative; the complete name(s) of the author(s); affiliation of the author(s); a running title of 40 characters or less; and the name and mail address to whom correspondence should be sent.

Page two should contain an abstract of not more than 150 words. This abstract should be intelligible by itself.

The main text should begin on page three and will ordinarily have the following arrangement:

Introduction: This should be brief and state the reason for the work in relation to the field. It should indicate what new contribution is made by the work described.

Materials and Methods: Enough information should be provided to allow other investigators to repeat the work. Avoid repeating the details of procedures that have already been published elsewhere.

Results: The results should be presented as concisely as possible. Do not use tables *and* figures for presentation of the same data.

Discussion: The discussion section should be used for the interpretation of results. The results should not be repeated.

In some cases it might be desirable to combine results and discussion sections.

References: References should be given in the text by the surname of the authors and the year. *Et al.* should be used in the text when there are more than two authors. All authors should be given in the Reference section. In the Reference section the references should be listed alphabetically. See below for style to be used.

RIZVI, S.S.H. 1986. Thermodynamic properties of foods in dehydration. In *Engineering Properties of Foods*, (M.A. Rao and S.S.H. Rizvi, eds.) pp. 133–214, Marcel Dekker, New York.

MICHAELS, S.L. 1989. Crossflow microfilters ins and outs. Chem. Eng. *96*, 84–91.

LABUZA, T.P. 1982. *Shelf-Life Dating of Foods*, pp. 66–120, Food & Nutrition Press, Trumbull, CT.

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.

Tables should be numbered consecutively with Arabic numerals. Type tables neatly and correctly as tables are considered art and are not typeset. Single-space tables. The title of the table should appear as below:

TABLE 1.
ACTIVITY OF POTATO ACYL-HYDROLASES ON NEUTRAL LIPIDS,
GALACTOLIPIDS AND PHOSPHOLIPIDS

Description of experimental work or explanation of symbols should go below the table proper.

Figures should be listed in order in the text using Arabic numbers. Figure legends should be typed on a separate page. Figures and tables should be intelligible without reference to the text. Authors should indicate where the tables and figures should be placed in the text. Photographs must be supplied as glossy black and white prints. Line diagrams should be drawn with black waterproof ink on white paper or board. The lettering should be of such a size that it is easily legible after reduction. Each diagram and photograph should be clearly labeled on the reverse side with the name(s) of author(s), and title of paper. When not obvious, each photograph and diagram should be labeled on the back to show the top of the photograph or diagram.

Acknowledgments: Acknowledgments should be listed on a separate page.

Short notes will be published where the information is deemed sufficiently important to warrant rapid publication. The format for short papers may be similar to that for regular papers but more concisely written. Short notes may be of a less general nature and written principally for specialists in the particular area with which the manuscript is dealing. Manuscripts that do not meet the requirement of importance and necessity for rapid publication will, after notification of the author(s), be treated as regular papers. Regular papers my be very short.

Standard nomenclature as used in the engineering literature should be followed. Avoid laboratory jargon. If abbreviations or trade names are used, define the material or compound the first time that it is mentioned.

EDITORIAL OFFICE: DR. D.B. LUND, *Journal of Food Processing and Preservation*, Dean of Agriculture and Life Sciences, Cornell University, 260 Roberts Hall, Ithaca, New York 14853-4203 USA.

JOURNAL OF FOOD PROCESSING
AND PRESERVATION VOLUME 19, NUMBER 6

CONTENTS