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JOURNAL
OF
FOOD
PROCESS
ENGINEERING

D.R. HELDMAN
and
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FOOD & NUTRITION
PRESS, INC.

VOLUME 8, NUMBER 3

QUARTERLY

JOURNAL OF FOOD PROCESS ENGINEERING

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All subscriptions and inquiries regarding subscription should be sent to Food & Nutrition Press, Inc., 155 Post Road East, P.O. Box 71, Westport, Connecticut 06881 USA.

One volume of four issues will be published annually. The price for Volume 8 is \$70.00 which includes postage to U.S., Canada, and Mexico. Subscriptions to other countries are \$82.00 per year via surface mail, and \$90.00 per year via airmail.

Subscriptions for individuals for their own personal use are \$50.00 for Volume 8 which includes postage to U.S., Canada, and Mexico. Personal subscriptions to other countries are \$62.00 per year via surface mail, and \$70.00 per year via airmail. Subscriptions for individuals should be sent to the publisher and marked for personal use.

The *Journal of Food Process Engineering* (ISSN 0145-8876) is published quarterly (March, June, September and December) by Food & Nutrition Press, Inc.—Office of Publication is 155 Post Road East, P.O. Box 71, Westport, Connecticut 06881 USA. (Current issue is June 1985.)

Second class postage paid at Westport, CT 06881.

POSTMASTER: Send address changes to Food & Nutrition Press, Inc., 155 Post Road East, P.O. Box 71, Westport, CT 06881.

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**FOOD & NUTRITION PRESS, INC.
WESTPORT, CONNECTICUT 06881 USA**

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ISSN 0145-8876

Printed in the United States of America

MEETINGS

August, 1986

8/13-8/16: 5th International Drying Symposium. MIT, Cambridge, Massachusetts. Contact: M. Karel, Dept. of Applied Biological Sciences, MIT, Cambridge, Massachusetts 02139.

8/19-8/22: International Symposium on Food and Biotechnology. Hilton Hotel, Quebec City, Canada. Contact: M. LeFebvre, Centre de recherche en nutrition. Universite Laval, Quebec, Canada G1K7P4.

8/24-8/27: National Meeting of the American Institute of Chemical Engineers. Sheraton Boston Hotel and Boston Marriott. Boston, Massachusetts. Food, Pharmaceutical and BioEngineering Division Program. Contact: Martin Okos, Department of Chemical and Agricultural Engineering. Purdue University, West Lafayette, IN 47907.

September, 1986

9/7-9/10: Meeting of Commission C-2, International Institute of Refrigeration. University of California, Davis, California. Contact IIR, University of California Meeting, American Frozen Food Institute, 1838 El Camino Reale, Suite 202, Burlingame, California 94010.

9/10-9/12: Recent Advances and Developments in the Refrigeration of Meat by Chilling. Bristol, UK. Contact: R.T. Moses, Faculty of Engineering, Queens Bldg., University of Bristol, Clifton, Bristol BS81TR.

9/22-9/24: International IUFOST Symposium on Optimal Utilization of Raw Materials in Food Production Under Limited Energy Supply. Cracow, Poland. Contact Dr. Antoni Rutkowski, Polish Academy of Science P.2101, 00-901 Warsaw, Poland.

9/29-10/3: Mache Vo '86—Food Engineering/Process Equipment. Jaabeurs Exhibition Complex Utrecht, Holland. Contact: International Exposition for Dairy and Food Processors. The Beverage Industry and Biotechnology, Jaarbeursplein, Utrecht—Holland, Postbus 8500, 3503 RM Utrecht, Holland.

October, 1986

10/7-10/9: Fifth International Conference on Packaging. Bristol, England. Contact: Grinnins, Packaging Division, Pira, Randalls Road, Leatherhead Surrey KT227RU England.

10/15-10/19: Tokyo Pack '86, Tokyo, Japan. Contact: S. Koshino, c/o Japan Packaging Institute, Honshu Building, 12-8, Ginza 5-Chome, Chuo-Ku, Tokyo 104, Japan.

November, 1986

11/2–11/7: Winter Annual Meeting of the American Institute of Chemical Engineers. Fountainbleu Hilton and Edon Eoc Hotels, Miami Beach, Florida. Food, Pharmaceutical and Bioengineering Division Program. Contact: J.L. Rossen, Engineering R&D, Kraft, Inc., 801 Waukegan Road, Glenview, IL 60025.

11/12–11/13: International Symposium on Automatic Control and Optimization of Food Processes. Paris, France. Contact: J.J. Bimbenet, 1, Avenue Des Olympiades, F91305 Massy, France.

11/13–11/19: International Symposium of Food Working Party of the European Federation of Chemical Engineering. Paris, France. Contact: V. Reynaud, Salon Du Gia, 42, Rue Du Louvre, F-75001, Paris, France.

December, 1986

12/16–12/19: Winter Meeting of the American Society of Agricultural Engineers. Hyatt Regency Hotel, Chicago, IL. Contact: M.A. Purschwitz, American Society of Agricultural Engineers, 2550 Niles Road, P.O. Box 410, St. Joseph, MI 49085.

CONTENTS

Meetings	v
Effect of Different Tube Materials on the Steady Shear Tube Flow of Semi-Solid Foods	
M. DERVISOGLU and J.L. KOKINI	137
Water Absorption in Cereal Grains and Its Effect on Their Rupture Stress	
E.U.U. ITUEN, J.P. MITTAL and J.S. ADEOTI	147
Activity Coefficients of Aroma Compounds and Water Activity in Model Systems	
A. VOILLEY	159
The Effects of Gas Injection on the Efficiency of Thermal Energy Utilization in Spray Drying	
D.E. ROMERO-FERRER, C.H. AMUNDSON and C.G. HILL, JR.	171

EFFECT OF DIFFERENT TUBE MATERIALS ON THE STEADY SHEAR TUBE FLOW OF SEMI-SOLID FOODS

M. DERVISOGLU and J. L. KOKINI¹

*Rutgers University
Food Science Department
Cook College
New Jersey Agricultural Experiment Station
New Brunswick, New Jersey 08903*

Submitted for Publication August 16, 1985
Accepted for Publication November 27, 1985

ABSTRACT

The effect of different tube materials was studied using galvanized steel, PVC, teflon and glass capillaries on tomato paste, apple sauce, ketchup and mustard as typical semi-solid food materials. In the shear rate range of 10 to 1000 s⁻¹ studied apple sauce and mustard showed the most pronounced effect which was wall material and shear rate dependent.

INTRODUCTION

Generation of steady shear flow data for semi-solid foods is complicated due to effects such as time dependency, (Dzuy and Boger 1983; Kraynik and Showalter 1981; Figoni and Shoemaker 1981; Kokini and Dickie 1981) wall effects, slip and wall pinch and secondary flows that arise at relatively small shear rates in narrow gap geometries. A study of the flow properties of ketchup, mustard, apple sauce and tomato paste over a wide shear rate range using both narrow gap and tube viscometers revealed that the

¹Direct correspondence to Dr. J. L. Kokini, Department of Food Science, Rutgers University, P.O. Box 231, New Brunswick, New Jersey 08903.

data could be superimposed and the best correlations of the data were obtained with a model involving a yield stress, in particular with the Herschel-Bulkley Model over a wide shear rate range (Dervisoglu and Kokini 1986a). The wall effect in the tubular flow of these materials was also studied, and it was concluded that the steady shear flow data obtained were strongly affected by the wall effect (Dervisoglu and Kokini 1986b). It was further shown that this effect was due to apparent slip. Correction of the data produced a master curve which was independent of tube diameter.

The aim of the present study is to examine the effect of different wall surface characteristics of tubes made from different materials (galvanized steel, PVC, teflon and glass) on the steady shear tube flow data of ketchup, mustard, apple sauce and tomato paste. This is important because the food industry uses a variety of pipe materials and often design of flow processes does not take into account changes in frictional behavior of food materials due to surface characteristics. Furthermore, selection can be optimized based on the pipe wall material which generates the minimum friction.

EXPERIMENTAL

The steady shear flow data on ketchup, mustard, apple sauce and tomato paste using galvanized steel, PVC, teflon and glass tubes were generated with a custom built tube-flow experimental set-up. The detailed description of the set-up is given elsewhere (Dervisoglu and Kokini 1986a). The diameters of the tubes used were close to each other in order to minimize differences in flow data resulting from wall effects (0.65 cm, 0.62 cm, 0.67 cm and 0.78 cm for galvanized steel, PVC, teflon and glass tubes, respectively). A long entrance region of 90D was allowed to minimize the entrance effects and pressure drop measurements were taken over a distance of 65D with each tube in the shear rate range of 10s^{-1} to 3000s^{-1} . The results are the averages of two experiments for each material. Wall shear stress was calculated using:

$$\tau_w = \frac{\Delta PR}{2L}$$

and wall shear rate was calculated using:

$$\dot{\gamma} = - \frac{8\bar{V}}{D} \left[\frac{3n+1}{4n} \right]$$

which also involves the Rabinowitch-Mooney Correction (Bird *et al.* 1976; Dervisoglu and Kokini 1986a). Flow was laminar in all cases. This was ensured by calculating the Reynolds number. The Reynolds number was below 2100 in all cases.

RESULTS AND DISCUSSION

The shear stress versus shear rate data obtained using tubes made of galvanized steel, PVC, teflon and glass with close diameters and identical L/D ratios are shown in Fig. 1 to 4 for ketchup, mustard, apple sauce and tomato paste respectively, in the shear rate range of 10 to 3500 s⁻¹. The upper limit of this range corresponds to what is usually observed in flow processing operations. The flow curves indicate that the wall shear stresses measured using the galvanized steel tube are significantly larger than those measured using PVC, teflon and glass for all four semi-solid foods studied. This clearly shows that the surface properties of the tube wall affect the drag at the wall. All flow curves could be simulated using the power-law model. The parameters *m* and *n* are reported on each figure as a function of tube material studied. It can be seen in each case that the value of *n* does not change significantly, showing that the nature of the surface does not affect the shear thinning behavior of each material. The fact that the value of *n* is very small in all cases suggests that most of the shear occurs in a narrow layer next to the wall and that the flow behavior approaches that of plug flow.

The values of *m* on the other hand vary more than the variation observed in the values of *n* suggesting that the nature of the wall surface results in an effective thinning of each food material.

Among relevant surface properties surface roughness and wetting properties should be the two most important. These have not been investigated in detail in this study.

The ratio of the shear stress measured for each tube material to the shear stress measured with the galvanized steel tube was plotted against the shear rate on semi-logarithmic coordinates where shear stress ratio was plotted as the linear coordinate. Such plots are shown for ketchup, mustard, apple sauce and tomato paste in Fig. 5 to 8. In these figures the effect of surface properties is magnified and it is clearly seen that the particular material selected affects the level of shear stress generated at the wall of the pipe.

A common observation for all materials is the fact that glass gives the lowest shear stress. This might be due to the fact that glass is the smoothest of all the materials used. Furthermore, the reduction in wall shear stress

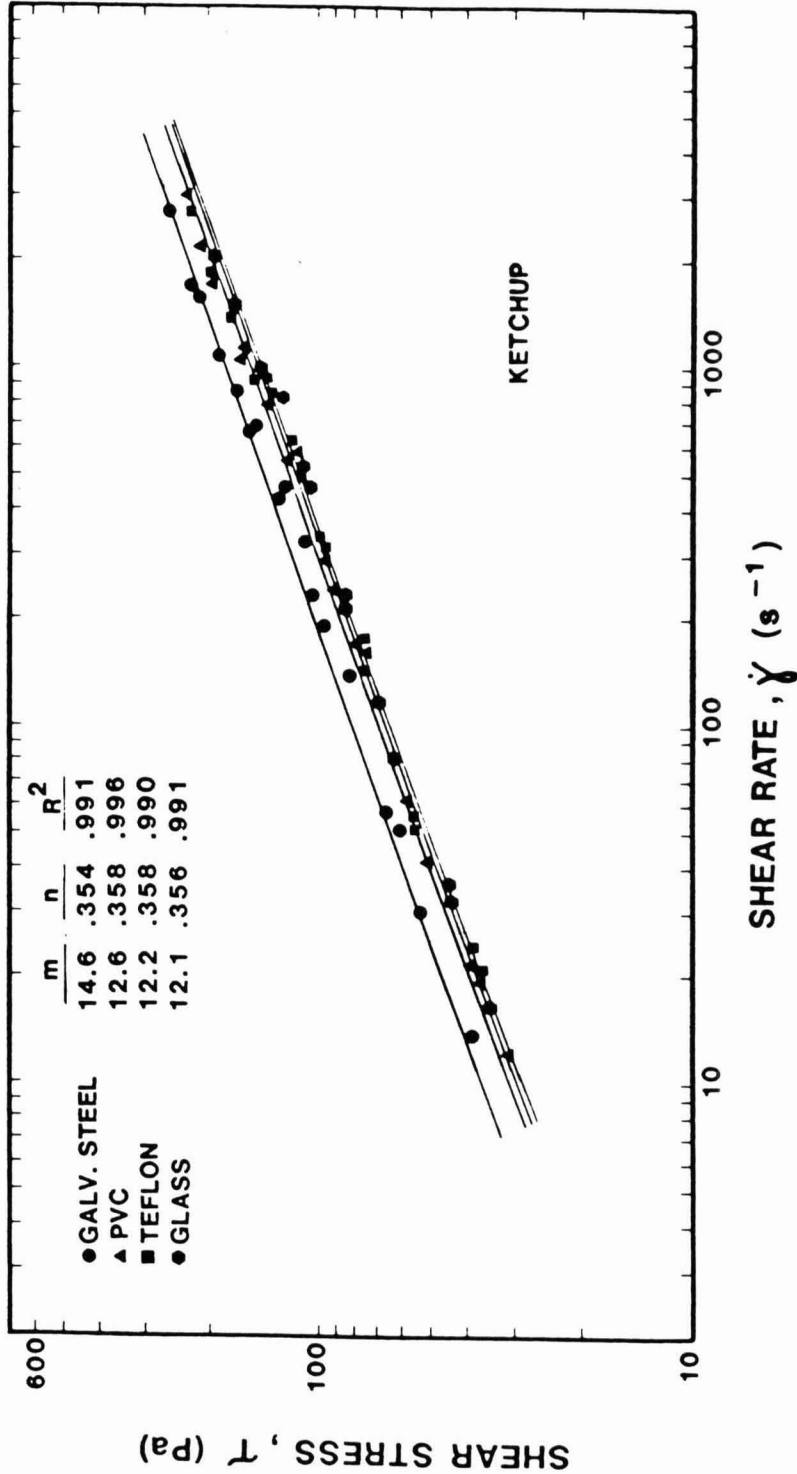
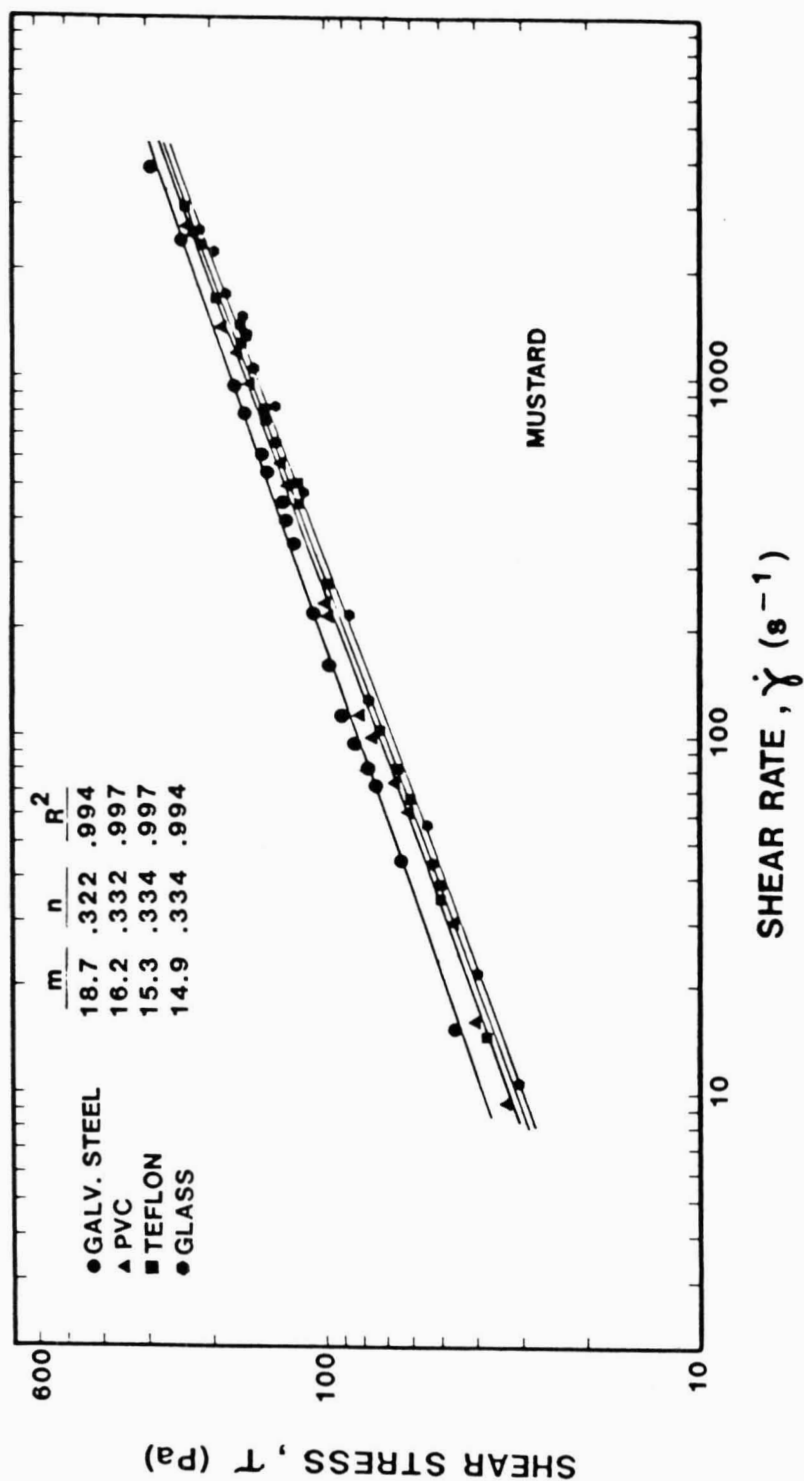


FIG. 1. TUBE FLOW DATA OBTAINED FOR KETCHUP USING TUBES MADE OF DIFFERENT MATERIALS



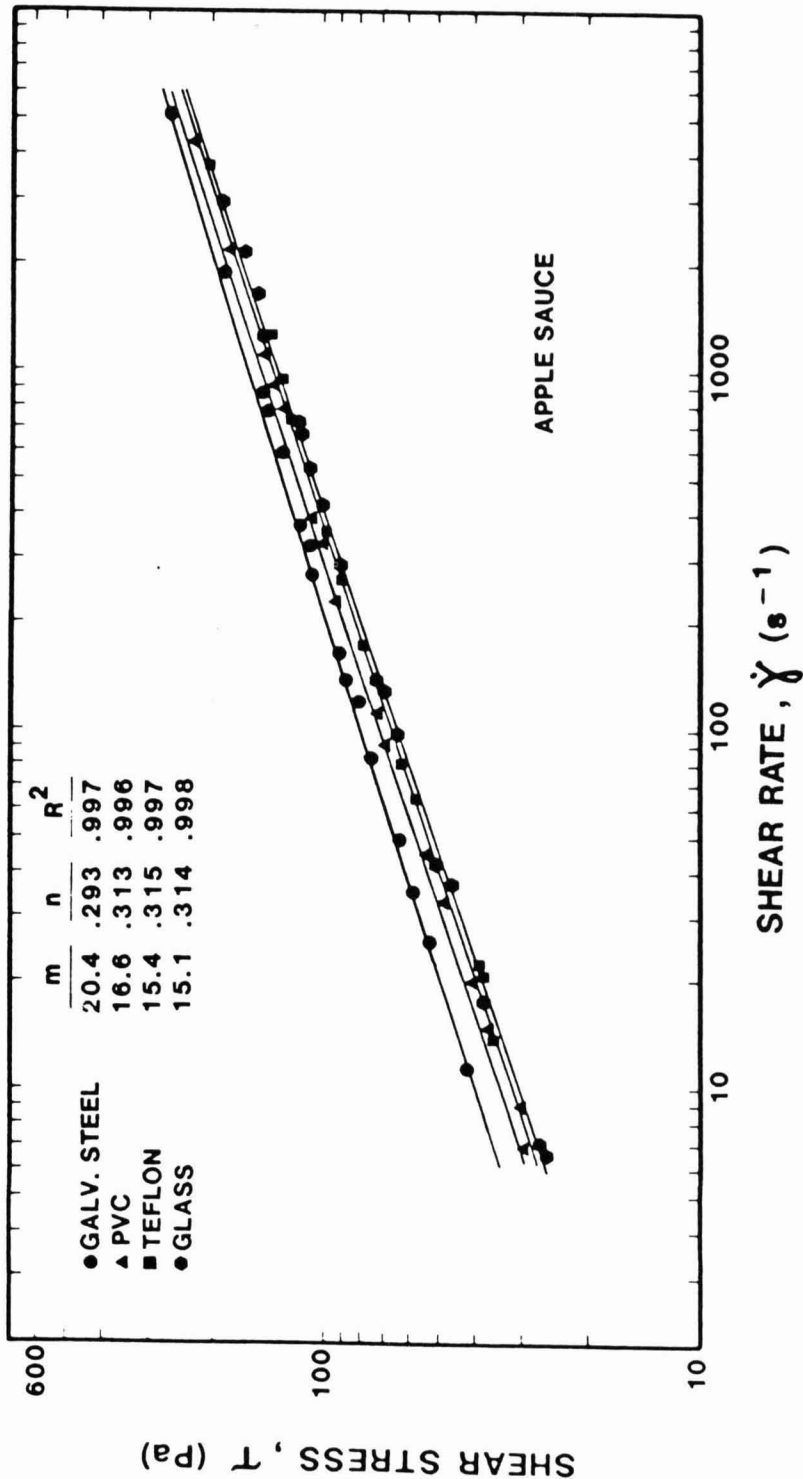


FIG. 3. TUBE FLOW DATA OBTAINED FOR APPLE SAUCE USING TUBES MADE OF DIFFERENT MATERIALS

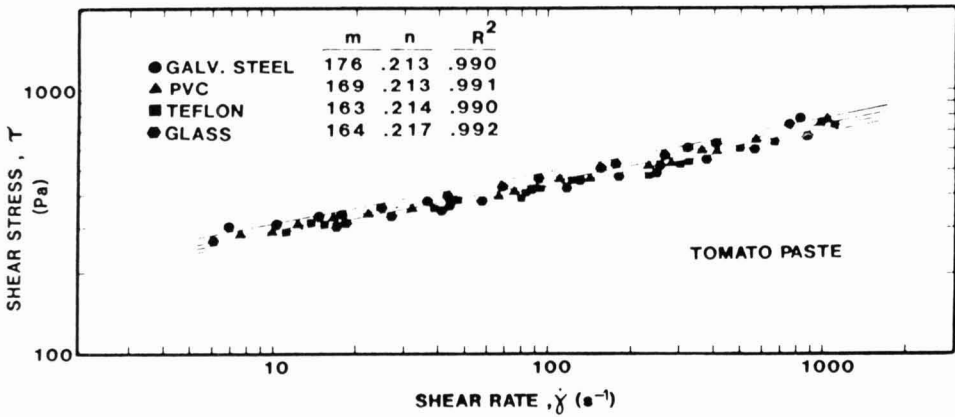


FIG. 4. TUBE FLOW DATA OBTAINED FOR TOMATO PASTE USING TUBE MADE OF DIFFERENT MATERIALS

is highest at the lowest shear rates for all materials except for the tomato paste and is less as the shear rate is increased. Specifically, for apple sauce in glass in the shear range of 10 to 30 s^{-1} the reduction in wall shear stress is about 21% relative to galvanized steel and decreases to about 15% as the shear rate is increased to 1000 s^{-1} . Teflon follows this trend closely and gives reductions which are very close in magnitude to those obtained

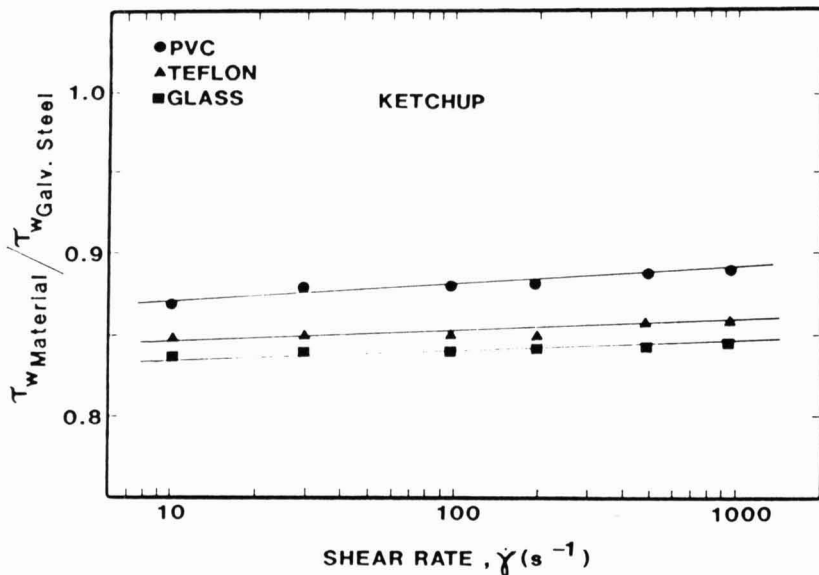


FIG. 5. COMPARISON OF THE EFFECT OF DIFFERENT TUBE MATERIALS ON THE STEADY SHEAR FLOW OF KETCHUP

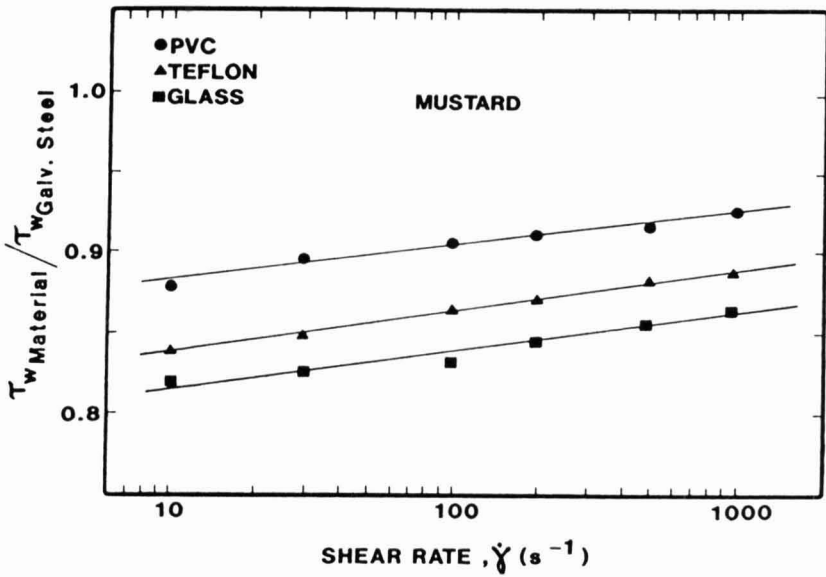


FIG. 6. COMPARISON OF THE EFFECT OF DIFFERENT TUBE MATERIALS ON THE STEADY SHEAR FLOW OF MUSTARD

with glass. Reductions obtained with PVC on the other hand are significantly lower as seen in Fig. 7. The highest reduction which could be ob-

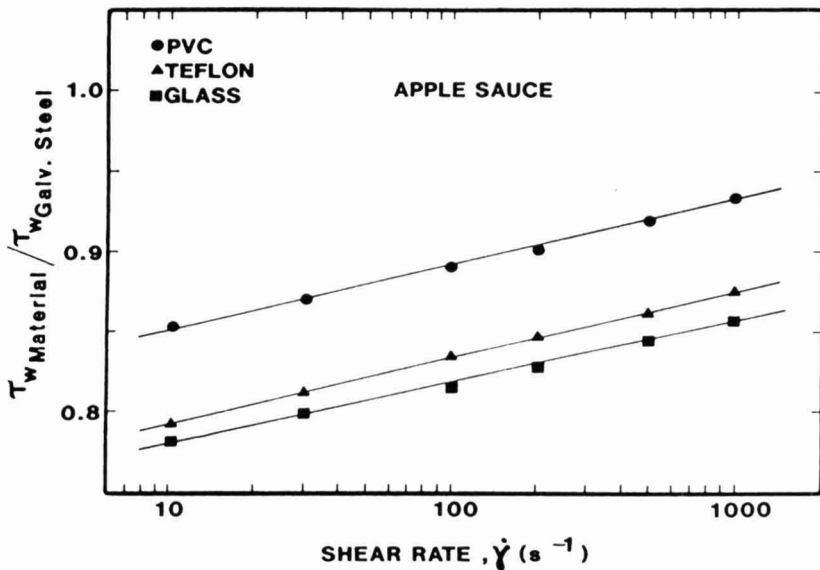


FIG. 7. COMPARISON OF THE EFFECT OF DIFFERENT TUBE MATERIALS ON THE STEADY SHEAR FLOW OF APPLE SAUCE

tained was 15% at a shear rate of 10 s^{-1} which was reduced to 10% at a shear rate of 1000 s^{-1} .

For mustard in Fig. 6 reductions in wall shear stresses obtained are less than those observed with apple sauce. With glass these values range from 18% to 13% going from 10 to 1000 s^{-1} . In this case reductions obtained with teflon do not follow those obtained with glass as closely as in the case of apple sauce. PVC gives as before the least pronounced reductions.

In ketchup and tomato paste in Fig. 5 and 8 the differences in the levels of reduction obtained with PVC, teflon and glass are less pronounced and in the case of tomato paste the differences observed are almost within the range of experimental error. This might be due to the fact that tomato paste and ketchup adhere to the wall surface better than apple sauce and mustard. Apple sauce is the most nonhomogeneous of all the materials studied. It was shown that (Kokini and Dervisoglu 1986b) wall slip for this material was highest. The fact that the reduction in wall shear stress on apple sauce decreases with increasing shear rates might be explained through the possible thinning of the lubricant layer, thus making any level of roughness significant and reducing the difference among surfaces. Nevertheless, the reductions going from galvanized steel to glass are of the order of 16% in the case of ketchup and 6% in the case of tomato paste.

In conclusion, for all the semi-solid foods studied, wall shear stress significantly depends on the tube material selected and that the lowest shear

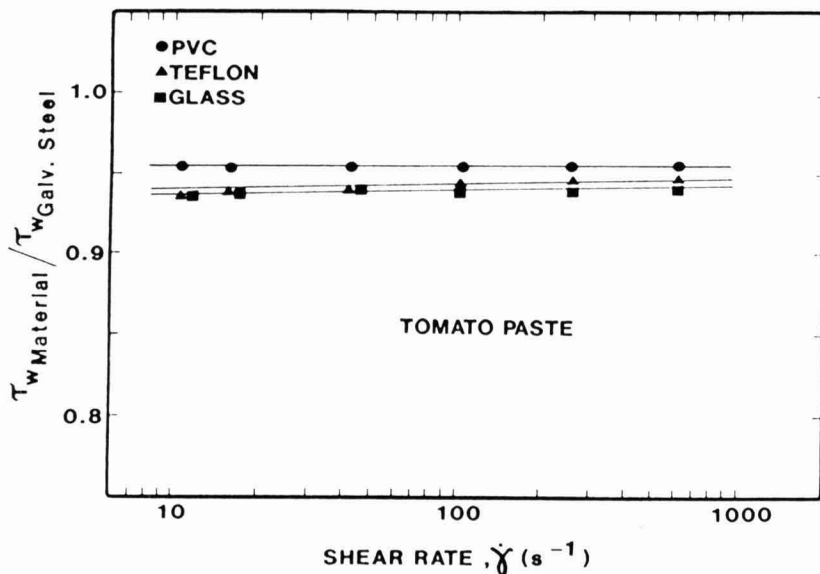


FIG. 8. COMPARISON OF THE EFFECT OF DIFFERENT TUBE MATERIALS ON THE STEADY SHEAR FLOW OF TOMATO PASTE

stress measurements are obtained using glass tubes. Teflon and PVC tubes give the second and third lowest shear stress.

ACKNOWLEDGMENT

This paper D-10522-3-1985 of the New Jersey Agricultural Experiment Station. This research was supported by the Campbell Soup Company and their support is greatly appreciated.

REFERENCES

- DERVISOGLU, M. and KOKINI, J. L. 1986a. Steady shear rheology and fluid mechanics of four semi-solid foods. Submitted to J. Food Sci.
- DZUY, N. Q. and BOGER, D. V. 1983. Yield stress measurement of concentrated suspensions. J. Rheol. 27, 321.
- FIGONI, I. P. and SHOEMAKER, F. C. 1981. Characterization of the structural breakdown of foods from their flow properties. J. Texture Stud. 12, 287.
- KOKINI, J. L. and DERVISOGLU, M. 1986b. Wall effects in the laminar pipe flow of four semi-solid foods. Submitted to J. Rheology.
- KOKINI, J. L. and DICKIE, A. 1981. An attempt to identify and model transient viscoelastic flow in foods. J. Texture Stud. 8, 1985.
- KRAYNIK, A. M. and SHOWALTER, W. R. 1981. Slip at the wall and extrudate roughness with aqueous solutions of polyvinylalcohol and sodium borate. J. Rheol. 25, 95.

WATER ABSORPTION IN CEREAL GRAINS AND ITS EFFECT ON THEIR RUPTURE STRESS¹

E. U. U. ITUEN

*Agricultural Engineering Workshop
Ekpri Nsukara
Ministry of Agriculture
Uyo (Cross River State)
Nigeria*

J. P. MITTAL²

*Project Coordinator
All India Coordinated Research Project on
Energy Requirements in Agricultural Sector
College of Agricultural Engineering
Punjab Agricultural University
Ludhiana-141 004, India*

and

J. S. ADEOTI

*Department of Agricultural Engineering
PMB 1044
Ahmadu Bello University
Zaria (Nigeria)*

Submitted for Publication July 1, 1985
Accepted for Publication October 16, 1985

ABSTRACT

A study on water absorption characteristics of the selected cereal grains was conducted. It was found that well dried maize, sorghum and millet

¹The work forms part of the senior author's Master of Engineering degree program at the Ahmadu Bello University, Zaria (Nigeria).

²Author to whom the correspondence should be addressed.

grains take about 96, 48 and 24 h, respectively, to reach their water absorption capacities (water absorption saturations). Millet had the highest rate of water absorption as well as the total water absorbed. The rate of water absorption in sorghum was higher than in maize but maize grains imbibed more water than sorghum.

Rupture stress of the grains and its variation with moisture content was also investigated. The rupture stress of the grains was seen to decrease with increase in moisture content except for maize which showed a rapid rise only at the onset of the increase in moisture content.

INTRODUCTION

In Nigeria, wet and dry grindings are performed for making of such recipe as 'tuwo' from dry flour and 'ogi' from wet products (Ituen *et al.* 1985). In a survey, it was found that about 0.5 tons of cereal grains is ground each day out of which the wet grinding accounts for about 16.0% (Mittal and Kaul 1983).

In Nigeria, the level of water in soaked grains for the making of 'Ogi' and other recipes is determined arbitrarily. Soaking of grain softens it and the grinding becomes comparatively easier. However, the level of moisture in soaked grains greatly effects the wet grinding characteristics (Ituen *et al.* 1985). To make a consistent product and for designing an efficient wet grinding device, it is necessary to study the water absorption behavior of cereal grains and its effect on the rupture strength of the grain in order to optimize the soaking time.

THEORETICAL CONSIDERATIONS

In biological materials, the moisture is absorbed in two ways: (1) capillary absorption, and (2) molecular absorption (Mohsenin 1970). Capillary absorption occurs in complex cellular capillary structures such as timber where the distance between cell walls is greater than that of the molecular structure. Molecular absorption occurs when the water molecules are bound to specific points in the molecular structure of the material. The distance between the water molecule and the cell wall is very small (of the order of 1×10^{-7} m), thus resulting in a force of attraction large enough to draw the water into the micellar network of the cell wall (Keey 1972). Mohsenin (1970) pointed out that the main cause of swelling in hygroscopic solids is molecular absorption.

Chung and Pfoest (1967) indicated that the starch in corn kernels contains more polar sites for the attraction of water molecules than the cellulose.

Therefore, larger amounts of water is absorbed by starchy materials than cellulose materials. The water absorption in grains depends upon three factors namely, (1) the temperature of soaking water, (2) the hardness of water, and (3) the storage conditions of the grains (Oyeleke 1981).

Kunze and Choudhury (1972) found that the rice kernels, when exposed to a higher relative humidity atmosphere or moisture absorption environment, do not fissure immediately but require a lapse of time called the "retardation time." The retardation time is dependent on the exposure, relative humidity of the atmosphere, variety and form of grain crop. It was found that brown rice required more time than polished rice for an initial fissuring response because polished rice absorbed moisture faster than brown rice.

Researchers have established a critical moisture content of rice above and below which it will not fissure. The specific moisture level at which this behavioral changes occur depends on the variety and type of rice as well as on the temperature of the environment. Stahel (1935) suggested 14% as the critical moisture level for rice. Rhind (1962) suggested that starch gel in rice is brittle below 15% moisture content but plastic at higher moisture levels. Brekke (1968) found that during tempering process (soaking in water) of corn, the highest rate of stress crack formation usually occurs between 0.5 and 2 h at temperatures ranging from 18.3° and 29.4°C.

The tensile strength of rice increased with the increase in time of storage in a given environment probably due to: (1) the relaxation of residual stress which might have developed due to maturity of grain in the field, field drying of grain and effect of subsequent environmental changes on the grain, and (2) chemical or biological changes within the kernels (Kunze and Choudhury 1972).

MATERIALS AND METHODS

Selection of Materials

Maize (variety: TZB), sorghum (variety: Short Kaura) and millet (variety: Ex-Borno) were selected because of their popularity in the Nigerian diets and also because of current research interest. Maize grains were obtained from the National Seed Service whereas sorghum and millet from the Institute for Agricultural Research, both of Samaru, Zaria.

Experimental Procedure

Water Absorption. A piece of mosquito netting was wetted by the water and its weight was taken with the help of a weighing balance (Model: Mettler PN 1210; accuracy: 0.01 g). A sample of 100 g grains was tied

in the netting and the netting with grains was immersed in a beaker containing ordinary tap water at a temperature of 28°C. Three replications were made.

Weighing of the soaked grains started after 5 min of soaking. In this process, the netting was removed from the water, shaken and sponged to drain off any free water on the surface of the netting and the grains. Water absorbed by the grain with respect to soaking time was determined by subtracting the original weight of grains from the weight of the water-absorbed grains. Soaking of grains in water continued till they stopped absorbing water further (i.e. the moisture absorption capacity was reached). The temperature and the relative humidity of the environment were recorded. The moisture content of the soaked grains was determined as per ASAE Standard S.352 (ASAE Year Book 1979/80).

Rupture Stress. Separately, grains of maize, millet and sorghum were soaked in water at the same time the water absorption experiment started. Every time the moisture absorption measurement was taken, ten grains were ruptured with the help of a plunger of 5 mm diameter in a rupture strength tester (Model: Kiya Seisakusho). The indicated rupture strength was recorded. The contact area was calculated as per ASAE recommendation ASAE R 368 (ASAE Year Book, 1979/80).

RESULTS AND DISCUSSION

Water Absorption by Maize, Sorghum and Millet Grains

Table 1 gives the data on water absorbed by all the selected cereal grains and their moisture content at various soaking times. Figure 1 shows the amount of water absorbed by maize, sorghum and millet grains against soaking time. It can be seen from Fig. 1 that the quantity and rate of water absorption was maximum for millet. Maize absorbed more water than sorghum but comparatively at a slower absorption rate. Oyeleke (1981) had a curve for water absorption in cowpeas similar to Fig. 1 and showed that a constant, called hydration coefficient, can be calculated from water absorption of the grain by using Eq. 1 given below.

Hydration Coefficient (h.c.) =

$$\frac{\text{Initial weight of grain, g} + \text{weight of imbibed water, g}}{\text{Initial weight of grain, g}} \quad (1)$$

This hydration coefficient can be used to indicate the water absorption capacity of the grains. In this case, the amount of water absorbed at satura-

Table 1. Water absorption and moisture content of maize, sorghum and millet grains as affected by soaking time
 Relative Humidity 11.90% Temperature of water: 28°C

Soaking Time, h	Water Absorbed, g		Final Moisture content(v.b.), %	
	Maize	Sorghum	Millet	Millet
0.00	0.00	0.00	0.00	5.19
0.08	6.80	12.52	17.59	11.24
0.25	10.05	15.71	22.62	13.84
0.50	10.96	19.86	25.74	14.56
1.00	14.20	24.13	29.81	16.99
2.00	17.23	29.23	35.87	19.14
4.00	22.47	35.49	44.12	22.59
8.00	31.43	41.63	50.32	27.87
10.00	34.87	43.83	52.58	29.70
20.00	43.69	47.07	56.41	34.02
24.00	44.95	47.86	59.04	34.60
30.00	46.68	48.02	58.62	35.36
34.00	47.88	47.98	57.50	35.90
48.00	50.78	49.20	58.61	37.13
54.00	51.94	49.16	58.42	37.61
69.00	53.96	49.17	57.68	38.42
72.00	54.31	48.44		38.57
78.00	54.03			38.46
96.00	56.95			39.50
102.00	54.88			38.79

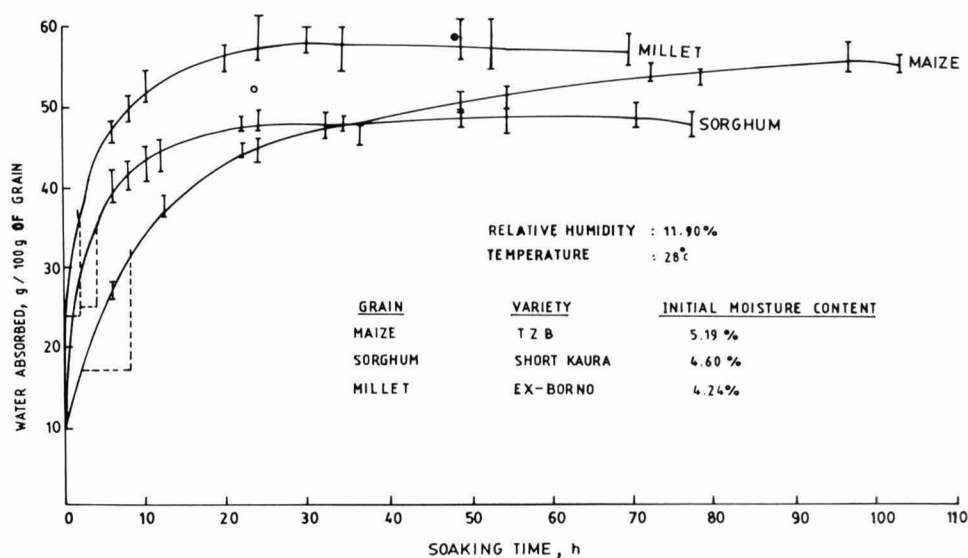


FIG. 1. WATER ABSORPTION OF CEREAL GRAINS
AS AFFECTED BY SOAKING TIME

tion is to be considered as the weight of the imbibed water. Therefore, the hydration coefficient (h.c.) of these cereal grains may be calculated as follows:

$$\text{Maize, h.c.} = \frac{156.95 \times 100}{100} = 156.95$$

$$\text{Sorghum, h.c.} = \frac{149.20 \times 100}{100} = 149.20$$

$$\text{Millet, h.c.} = \frac{159.04 \times 100}{100} = 159.04$$

Thus, the hydration coefficient for millet is highest followed by maize and sorghum. Millet and sorghum attained their maximum capacity for water absorption in about 24 and 48 h of soaking, respectively. Maize, though with the lowest rate of water absorption, continued to absorb water up to about 96 h of soaking. That, maize takes so long a time to reach saturation in water absorption conforms with Leonard and Martin (1963) who indicated that maize grains in a starch industry are usually steeped in water for about 40 to 60 h before grinding.

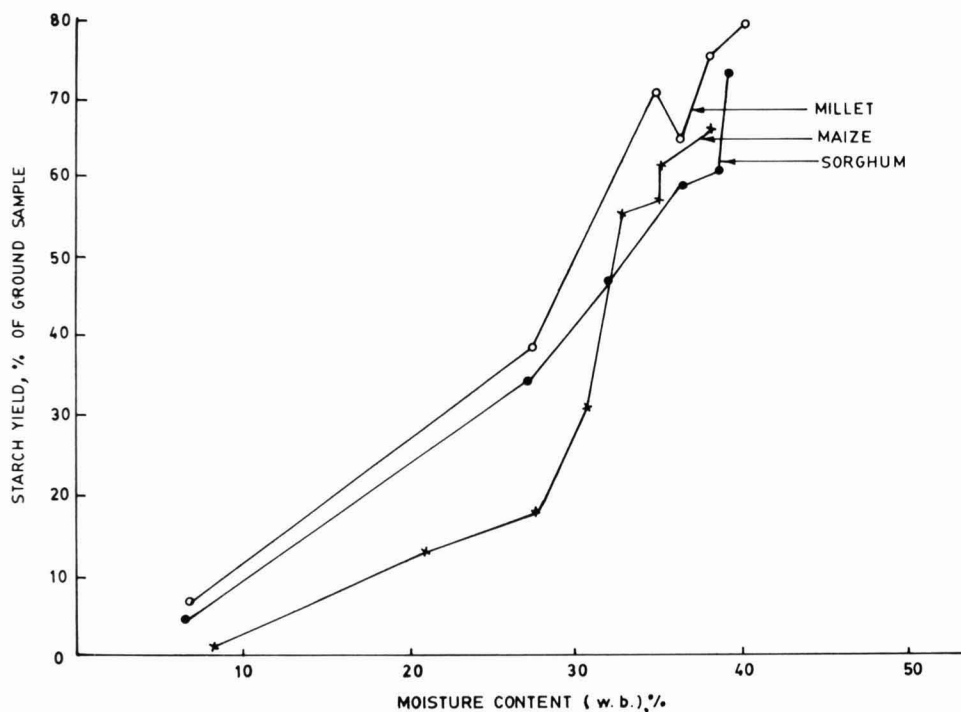


FIG. 2. EFFECT OF MOISTURE CONTENT ON STARCH YIELD

Figure 2 shows the starch yield (pan fraction) at different moisture contents. It can be seen that the starch was highest for millet followed by sorghum and maize. The starch content might have been responsible for their different rates of water absorption. Mohsenin (1970) pointed out that when the distance between the water molecule and the cell wall becomes small enough, the force of attraction is large to draw the water into the micellar network of the cell wall. It could, therefore, be argued that the smaller the grain the smaller will be the said distances resulting in the greater force of attraction of moisture into the cell wall. Thus millet, the smallest of the three grains, might have had the highest force of moisture attraction, hence the highest rate of absorption followed by sorghum. The third point of consideration is that the moisture content of the grain affects the force of moisture attraction. It is known that the lower the moisture content the higher will be the force of moisture absorption. Millet grains had smallest moisture content followed by sorghum and maize. The rate of moisture absorption was, therefore, highest in millet followed by sorghum and maize.

Response Curve of the Water Absorption of Grains

The curve of the moisture content of maize, sorghum and millet is a response curve of the first-order systems equation given by the expression:

$$B_t = B_0 + B_r (1 - e^{-t/\tau}) \quad (2)$$

Where

B_t = total moisture content of the grain at time t

B_0 = initial moisture content of the grain

B_r = moisture content of the grain due to water absorbed

τ = time constant of the system, measures how fast the system responds to a disturbance

t = soaking time

At $t = 0$, $B_t = B_0$

At $t = \infty$, $B_t = B_0 + B_r = B_{\text{sat}}$

Where B_{sat} = moisture content of the grain at Saturation
= moisture content of the grain at moisture absorption capacity

Therefore, total moisture absorbed, $B_r = B_{\text{sat}} - B_0$

At $t = \tau$, $B_t = B_0 + B_r (1 - \frac{1}{e})$

$$\text{or } B_\tau = B_0 + B_r (0.632) \quad (3)$$

Similarly

$$\text{At } t = 2\tau, B_{2\tau} = B_0 + B_r (0.865) \quad (4)$$

$$\text{At } t = 3\tau, B_{3\tau} = B_0 + B_r (0.95) \quad (5)$$

$$\text{At } t = 4\tau, B_{4\tau} = B_0 + B_r (0.982) \quad (6)$$

$$\text{At } t = 5\tau, B_{5\tau} = B_0 + B_r (0.993) \quad (7)$$

$$\text{At } t = 6\tau, B_{6\tau} = B_0 + B_r (0.998) \quad (8)$$

$$\text{At } t = 7\tau, B_{7\tau} = B_0 + B_r (0.999) \quad (9)$$

The value of 4τ is often used as the time at which the variation is essentially over, since less than 2% of the change remains to occur. A curve

showing up to 4τ is a standard of time for a change to occur (Shearer *et al.* 1967).

The following systems equations were found for various grains:

$$\text{Maize: } B_t = 5.2 + 34.0 (1 - e^{-t/7}) \quad (10)$$

$$\text{Sorghum: } B_t = 4.6 + 31.7 (1 - e^{-t/1.7}) \quad (11)$$

$$\text{Millet: } B_t = 4.2 + 35.8 (1 - e^{-t/1.25}) \quad (12)$$

Figure 3 shows the response curve of moisture content of grain at different soaking times obtained from the above systems equation. The systems equation curve fit the moisture content data of the grain given in Table 1 rather well.

Table 2. Rupture stress of maize, sorghum and millet with change in moisture content during soaking

Soaking time (hrs)	Maize		Sorghum		Millet	
	Moisture content (w.b.), %	Rupture stress, $\frac{\text{N}}{\text{m}^2}$	Moisture content (w.b.), %	Rupture stress, $\frac{\text{N}}{\text{m}^2}$	Moisture content (w.b.), %	Rupture stress, $\frac{\text{N}}{\text{m}^2}$
0.0 (dry)	5.19	18.96	4.60	5.90	4.25	0.95
0.08	11.24	20.25	15.21	7.20	18.56	1.57
0.25	13.84	7.55	17.55	5.02	21.91	1.03
0.50	14.56	7.75	20.41	2.65	23.85	0.95
1.00	16.99	4.80	23.15	0.64	26.23	0.73
2.00	19.14	12.63	26.18	2.05	29.52	0.42
4.00	22.59	4.50	29.35	1.45	33.55	0.15
8.00	27.87	6.83	32.64	0.31	36.30	0.00
10.00	29.70	5.25	33.67	1.12	37.24	0.00
20.00	34.02	6.61	35.15	2.58	38.78	0.00
24.00	34.60	7.56	35.48	0.74	39.79	0.00
30.00	35.36	5.30	35.55	0.08	39.63	0.00
34.00	35.90	4.03	35.53	2.28	39.89	0.00
48.00	37.13	3.87	36.06	0.01	39.63	0.00
54.00	37.61	3.20	36.04	0.01	39.56	0.00
72.00	38.57	7.88	35.73	0.01		
96.00	39.60	4.97				
102.00	38.79	6.55				

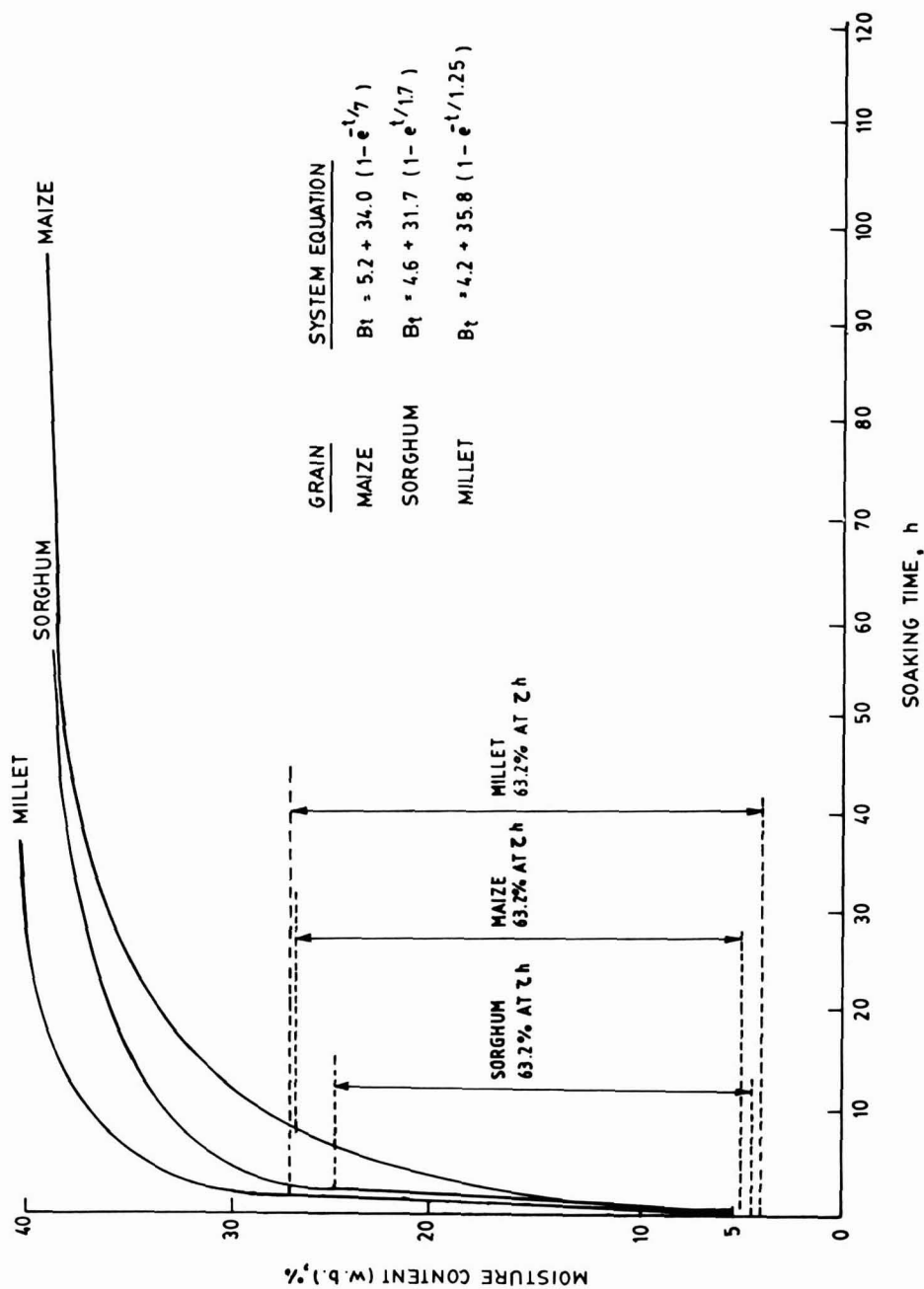


FIG. 3. RESPONSE CURVE OF MOISTURE CONTENT
VARYING WITH SOAKING TIME

Effect of Soaking on the Rupture Stress of Grain

Table 2 gives the rupture stress of grain at different moisture contents. Maize was observed to have the highest rupture stress followed by sorghum and millet. It was noticed that there was a sudden increase in the rupture stress of the grains in question just after soaking in water. The same phenomenon was observed by Kunze and Choudhury (1972) regarding increase in tensile strength of rice kernels. However, there was a general decline in the rupture stress as the moisture content of the soaked grains increased. The grains of large sizes required more strength for rupturing than those of small sizes. Grains with flat shape (like maize) required higher rupture stress than those having spherical or almost spherical shape. This phenomenon can be explained by stress, force and cross-sectional area relationship given below:

$$\varsigma = \lim_{A \rightarrow 0} F/A \quad (13)$$

Where ς = applied stress, Pa

F = applied force, N

A = cross sectional area perpendicular to applied force, m²

For large and flat shaped grains, the surface area in contact will be large which will result in comparatively small stress than for the grains smaller in size and spherical in shape.

Remarks: In the rupture strength tester, the final rupture strength reading is registered on the dial gauge. Therefore, it was not possible to show the point of rupture on the force-deformation curve. However, if the universal testing machine was available a more detailed analysis would have been carried out.

It may be further noted that the parameter known as toughness (the area under force-deformation curve) may give a better indication of kernel strength at different soaking time. This aspect should be studied in detail in future work.

CONCLUSIONS

The following conclusions were drawn from this research study.

(1) Millet has the highest rate and capacity of water absorption in comparison to maize and sorghum. Sorghum had a higher rate of water absorption than maize but the total amount of absorbed water was less than maize.

(2) The rupture strength of maize, sorghum and millet decreased with the increase in moisture content. However, the rupture strength of maize increased sharply at the start of soaking to a critical point before it started declining.

REFERENCES

- A.S.A.E. 1979/80 Yearbook. American Society of Agricultural Engineers, St. Joseph, MI.
- BREKKE, O. L. 1968. Stress Crack Formation in Tempering of Low Moisture Corn and Effect on Degerminator Performance. Nor. Reg. Res. Lab., USDA, Peoria, Illinois.
- CHUNG, D. S. and FOST, H. B. 1967. Absorption and Desorption of Water Vapour by Cereal Grains and Their Products. Part I, II, III. Trans. Amer. Soc. Agri. Eng. 10(4): 549.
- ITUEN, E. U. U., MITTAL, J. P., and ADEOTI, J. S. 1985. Particle Size Characterization of Selected Grains under Wet Grinding. J. of Food Process Engineering. 7 (1985): 287-505.
- KEEY, R. B. 1972. Drying Principles and Practices. Pergamon Press, Oxford.
- KUNZE, O. R. and CHOUDHURY, M. S. U. 1972. Moisture Absorption Related to Tensile Strength of Rice. Cereal Chemistry. 49: 684-696.
- LEONARD, W. H. and MARTIN, J. H. 1963. Cereal Crops, McMillan Publishing Co. Inc., New York.
- MITTAL, J. P. and KAUL, R. N. 1983. Performance Surveys on Village Level Grain Grinding in Selected Villages of Zaria Local Government. Nigerian Food Journal. 1(1): 109-114.
- MOHSENIN, N. N. 1970. Physical Properties of Plant and Animal Materials. Gordon and Breach Science Publishers, New York.
- OYELEKE, O. A. 1981. Processing of Cowpea and Other Materials for An Infant Food for Nigeria. Ph.D. Thesis. University of London, London.
- RHIND, D. 1962. Breaking of Rice in Milling. Tropical Agriculture. 39: 19.
- SHEARER, J. L., MURPHY, A. T., and RICHARDSON, H. B. 1967. Introduction to System Dynamics. Addison-Wesley Publishing Co., Reading, Massachusetts.
- STAHEL, G. 1935. Breaking of Rice in Milling of Paddy. Tropical Agriculture 12: 255.

ACTIVITY COEFFICIENTS OF AROMA COMPOUNDS AND WATER ACTIVITY IN MODEL SYSTEMS

A. VOILLEY¹

*Laboratoire de Biologie Physico-Chimique
ENS.BANA, C.U.M., 21000 Dijon, France*

Submitted for Publication May 15, 1985

Accepted for Publication August 29, 1985

ABSTRACT

One aim of this work was to measure the activity of water and aroma compounds in aqueous solutions simultaneously.

The volatilities of aroma substances at infinite dilution in aqueous solutions of polyethylene-glycols (PEG) were studied. The activity coefficients (γ_i^∞) of volatile compounds were measured by gas stripping (exponential dilution). This dynamic method also allowed the measurement of the water activity of these solutions. The results showed that:

(1) the influence of polyethylene-glycols on γ_i^∞ depended most strongly on the PEG mass fraction in the solution. The effect of the PEG molecular weight was not significant.

(2) γ_i^∞ increased as molecular weight and length increased for the homologous series of alcohols tested. This can be explained by entropic effects. Probably, the same effect occurs for other homologous series.

(3) γ_i^∞ for 2-propanone increased as temperature increased. Based on this relation, molar partial excess enthalpies of mixing were calculated for 2-propanone in an aqueous solution.

INTRODUCTION

In unit operations, the behavior of aroma compounds in food products depends strongly on their activity coefficients. In this study, activity coef-

¹Direct correspondence to Dr. A. Voilley, Universite de Dijon, Ecole Nationale Supérieure de Biologie Appliquée, a la Nutrition et a l'Alimentation, Campus Universitaire — 21000 Dijon, France.

ficients of volatiles at infinite dilution (γ_i^∞) were measured in model systems (aqueous solutions of polyethylene-glycols with defined molecular weights) by the inert gas stripping method described by Leroi *et al.* (1977). An equilibrium cell designed to permit measurements in highly viscous and foaming systems (Richon *et al.* 1984) was used. Water activity was measured by headspace analysis (Hachenberg 1975) at the same time as γ_i^∞ for aroma compounds. Thermodynamic models were described with the Gibbs Duhem equation in particular the groups contributions models (Derr and Deal 1969). These models were used to interpret the γ_i^∞ behavior. ASOG (Kojima and Tochigi 1979) can be used for polymers with more than 10 monomer groups. This model is based on the hypothesis (Wilson and Deal 1962) that the activity coefficient is the product of 2 terms: γ_i^f , which is caused by molecular differences in size and shape and γ_i^r , which represents interactions and is referred to as the residual term:

$$\gamma_i = \gamma_i^f \cdot \gamma_i^r$$

The details of calculations are described in Kojima and Tochigi 1979. This model was retained after a comparison of predictive values for other compounds obtained with ASOG and UNIFAC models (Sorrentino *et al.* 1986).

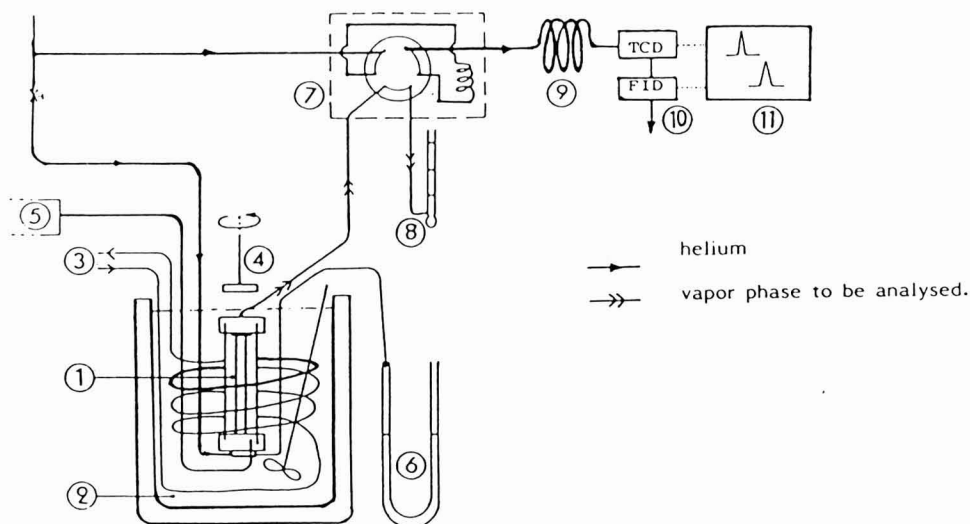
MATERIAL AND METHODS

The analysis system is shown in Fig. 1. The concentrations of water and aroma compounds in the vapor phase were measured simultaneously by gas-liquid chromatography using thermal conductivity (TCD) and flame ionization detectors (FID) in series. The temperature in the cell was exactly measured to allow corrections in calculating the activity coefficients of volatiles in the same manner as Richon *et al.* (1984) had used previously.

The method retained was the inert gas stripping method which allows rapid determination of accurate infinite dilution activity coefficients. The design of the equilibrium cell permitted work with viscous and foaming mixtures like aqueous solutions of polyethylene-glycols. Samples of vapor phases continuously flowing out from the cell were periodically analyzed through the gas-liquid chromatograph. In Fig. 2, the logarithm of volatile peak area, S , is plotted as a function of time t ; γ_i^∞ was determined from the slope.

Water activity (a_w) was expressed by:

$$a_w \approx \frac{P'}{P^0} \approx \frac{S'}{S^0}$$



- 1 - Exponential dilutor
- 2 - Thermostated bath
- 3 - Water flow
- 4 - Magnet
- 5 - Thermocouple
- 6 - Mercury manometer

- 7 - 6 way valves and oil bath at 100°C
- 8 - Flowmeter
- 9 - Gas liquid chromatograph
- 10 - 2 detectors - TCD
- FID
- 11 - Integrators, recorders

FIG. 1. SYSTEM FOR MEASUREMENT OF WATER ACTIVITY AND ACTIVITY COEFFICIENTS OF AROMA COMPOUNDS

where

P' = partial vapor pressure of water above the solution

P^0 = vapor pressure of pure water at the same temperature.

The peak areas (S' and S^0) for the same analyzed volume were assumed proportional to vapor pressure.

The chromatographic conditions were the following:

- (1) gas-liquid chromatograph Packard 427
- (2) two detectors in series, the first, TCD to analyze water, the second, FID to analyze aroma compounds
- (3) column Porapak Q, 0.7 m length, $3 \cdot 10^{-3}$ m internal diameter
- (4) injector temperature: 200 °C, detectors: 200 °C and column: 180 °C (isothermal)
- (5) rate flow for the vector gas (Helium): 60 ml/min.
- (6) integrator-calculator Hewlett-Packard 3380A.

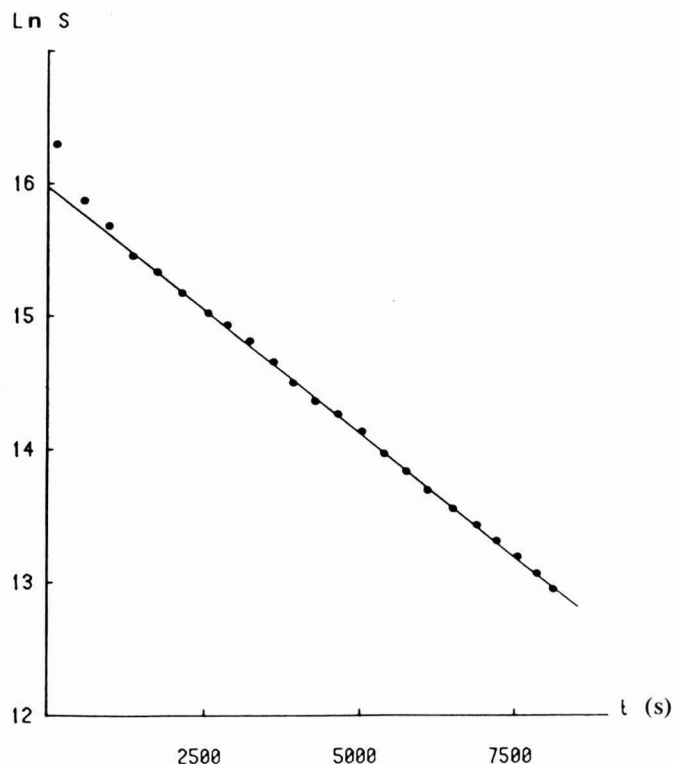


FIG. 2. LOGARITHM OF 2-PROPANONE (IN WATER) PEAK AREA AS A FUNCTION OF TIME

Under these conditions, activity coefficients of five volatiles in aqueous solutions of polyethylene-glycols (PEG) with different molecular weight, were measured. The characteristics of these compounds are given in Tables 1 and 2.

Table 1. Characteristics of volatiles

Name	Origin	Molecular weight	P_i^S at 298.15 K (mm Hg)
n-Propanol	Merck	60.09	21.25
2-Propanol	"	60.09	42.45
Hexanol	"	102.17	1
2-Propanone	"	58.68	232.5
Ethyl acetate	"	88.10	90

Table 2. Characteristics of PEG solutions

Name	Origin	Molecular weight	Viscosity (cP) of aqueous PEG solution (*) mass fraction (x100)		
			50	70	85
PEG 600	Merck	570- 630	13.7	48	86
PEG 1500	"	1400-1600	32.5	-	-
PEG 6000	"	5000-6000	179.6	-	-

*The viscosity was measured, at 298.25 K, with a coaxial cylinder viscometer (Rheomat 30 — Contraves).

RESULTS AND DISCUSSION

Repeatability

The results of a study of repeatability are given in Table 3. Ten to sixteen trials were done to calculate variation intervals (one sample was prepared each day). The variation coefficient for water activity (mean value = 0.954) was 0.9%. The precision was similar for 2-propanone activity coefficient.

Table 3. Repeatability of measurements a_w and γ^∞ 2-propanone

<u>a_w in aqueous solution of PEG (50 %) (298.15 K)</u>		
Sample	a_w	95 % variation interval
1	0.945	± 0.018
2	0.949	± 0.031
3	0.964	± 0.021
4	0.959	± 0.026
<hr/>		
<u>γ^∞ of 2-propanone</u>	γ^∞	95 % variation interval
in water (7 trials)	7.72	± 0.12
in aqueous solution of PEG (50 %) (3 trials)	8.0	± 0.12

Water Activity (and Activity Coefficient)

Table 4 gives the results of water activity for aqueous solutions of PEG 600 and 1500 at different concentrations. Our experimental results were

Table 4. a_w and γ_w of solutions of PEG 600 and 1500 (298.15 K)

Concentration % (mass/mass)	30	PEG 600 50	70	85	PEG 1500 50
Experimental value	0.97 ± 0.01	0.95 ± 0.01	0.92 ± 0.02	0.70 ± 0.02	0.95 ± 0.01
a_w (25°C) CHIRIFE (1980) *	0.98	0.92	-	-	-
NORRISH (1966)**	0.98	0.93	0.73	-	0.94
ASOG	0.97	0.93	0.81	0.58	0.94
$\left[\frac{a_w \text{ ASOG} - a_w \text{ EXP}}{a_w \text{ exp}} \right] (\%)$	0	- 2.1	- 12	- 17.7	- 1
γ_w (ASOG)	0.99	0.96	0.87	0.68	0.95

(*) measured with LUFFT technique (fiber hygrometer)

(**) calculated by NORRISH equation (1966) $a_w = x_w \exp(-K \cdot x_s)^2$
 x_w and x_s , respectively mole fractions of the water and of the solute K, constant

compared to those obtained by the ASOG predictive model and with results found in literature. The deviation from the ASOG values increased with an increase of the PEG concentration.

γ^∞ of Volatiles in Aqueous Solutions

Influence of the PEG. For 2-Propanone and Ethyl acetate, γ^∞ decreased with an increase in the mass fraction of PEG 600 (Table 5) and the consequent decrease in water activity at 298.15 K. At 313.15 K, γ^∞ of 2-Propanone also decreased in the same way at 298.15 K. For example, in 30% (m/m) PEG 600, γ^∞ of 2-Propanone was equal to 9.5 whereas in pure PEG it was 0.55. On the contrary Sorrentino *et al.* (1985) observed a slight increase of γ^∞ of 2-Propanone with an increase in mass fraction from 15 to 30% of PEG 6000, 10000 and 35000. The aqueous solution of PEG 600 seemed to chemically bind with volatiles. In this case, after a revision of the calculation taking into account the influence of hydroxyl terminal groups in the ASOG model (calculated by Kojima and Tochigi 1979), the predicted γ^∞ is approximately near the experimental value (Table 5 and Fig. 3). On the contrary, the effect of molecular weight of PEG on γ^∞ for 2-Propanone was negligible (Table 6).

Influence of the Volatile Characteristics. The variation of γ^∞ between n-Propanol and n-Hexanol showed that γ^∞ increased with volatile chain length in aqueous solutions of this homologous series (Table 7). The same phenomena had been observed by Buttery *et al.* (1969), Lebert and Richon (1984a) and Sorrentino *et al.* (1984) for homologous series of Ketones, esters and aldehydes. On the contrary, Allaneau (1979), Lebert and Richon (1984b) observed a decrease of γ^∞ of alcohols in presence of oil; this was due to the fact that the hydrophobic part of the volatile increase with an increase of chain length and there was an interactive effect not an entropic effect.

The difference between γ^∞ of n-Propanol and γ^∞ of 2-Propanol showed that branching decreased the activity coefficient. This variation and the increase of γ^∞ with the length could be explained by the variation of the entropic term of γ^∞ which increases when there is an increase in the molar volume of volatile compound (which depends on the length).

For the other aroma compounds tested, the results were similar to previously observed results. Voilley *et al.* (1977), for example, obtained an γ^∞ of 7.4 for 2-propanone in pure water at 298.15 K and Chandrasekaran *et al.* (1972) obtained a value of 65 for γ^∞ for Ethyl acetate. In the case of the 3-carbon chain the γ^∞ of acetone was less than the γ^∞ of alcohol which was less than the γ^∞ of ester; The γ^∞ of 2-propanone was one tenth as small as the γ^∞ of Ethyl acetate. This difference can

Table 5. Influence of the mass fraction of PEG 600 on γ^∞ for volatiles (298.15 K)

Mass fraction (%) of PEG 600		0	30	50	70	85	100
2-Propanone	(EXPERIMENTAL)	7.7	8.7 ± 0.2	7.6 ± 0.2	6.1 ± 0.2	3.5 ± 0.2	0,55
	(ASOG)(1)	8.0	8.1	8.2	8.3	7.9	-
	(ASOG)(2)	8.0	8.4	8.5	5.6	-	-
	$\left[\frac{(\text{ASOG}(2) - \text{EXP})}{\text{exp}} \right] \%$	+ 3.9	+ 3.4	+ 12	- 8.2	-	-
Ethyl acetate	(EXP)	77.0	66 ± 2	54.9 ± 0.6	24 ± 2	8.7 ± 0.4	-
	(ASOG)(1)	81.1	89.6	87.0	75.8	56.9	-
	(ASOG)(2)	81.1	87.4	78.5	42.5	-	-
	$\left[\frac{(\text{ASOG}(2) - \text{EXP})}{\text{exp}} \right] \%$	+ 5.3	+ 32.0	+ 43.0	+ 77.0	-	-

ASOG (1): calculated with ASOG (parameters determined by Sorrentino *et al.* 1986).

ASOG (2): calculated with ASOG modified to take terminal hydroxyl groups into account.

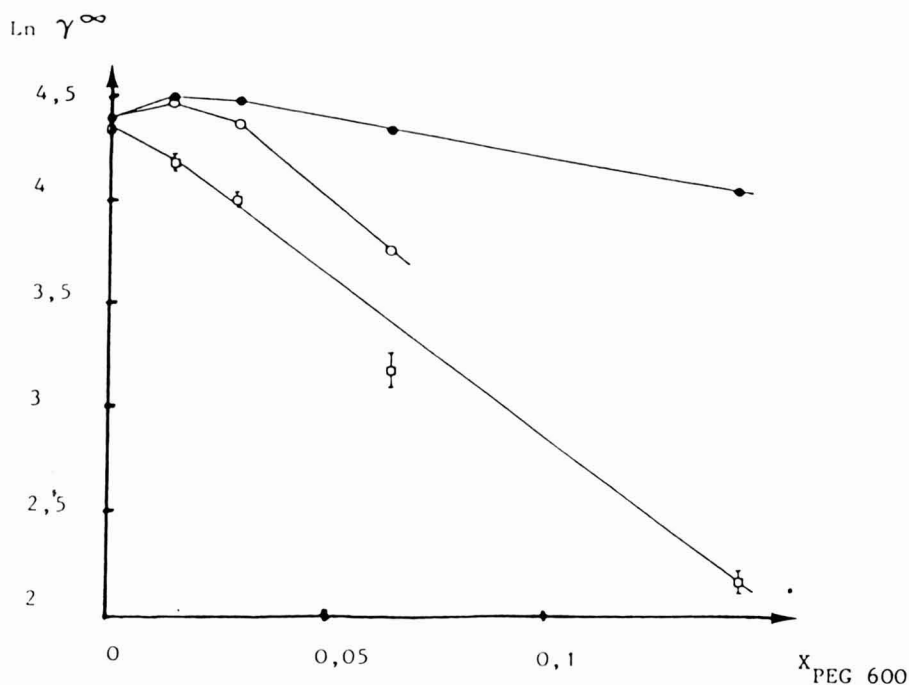


FIG. 3. EXPERIMENTAL VALUES OF $\text{Ln } \gamma^\infty$ AS A FUNCTION OF MOLAR FRACTION OF PEG 600 AT 298.15 K FOR ETHYL ACETATE

- \square experimental values
- \bullet predicted values (calculated with ASOG)
- \circ predicted values (calculated with modified ASOG)

Table 6. γ^∞ values of 2-Propanone in PEG's solutions (30% w/w)

Mean molecular weight of PEG					
PEG	:	600	6000	10000	35000
γ^∞ (298.15 K):		8.7 ± 0.2	8.7	8.4	8.4

be explained partially by the fact that the Ethyl acetate molecule is physically larger than the 2-propanone; most likely the carbonyl in 2-propanone interacts strongly with water molecules.

The ASOG predictions were not identical to the experimental values, which depended on the nature of volatile and substrates. The influence of the hydroxyl group in PEG 1500 was not so marked as in PEG 600 because the hydroxyl terminal groups occupy a smaller fraction of the molecule in PEG 1500.

Table 7. γ^∞ values of volatiles in water and aqueous solutions of PEG 1500 (298.15 K)

<div> <div> Volatile compound γ^∞ </div> </div>	n-Propanol	2-Propanol	Hexanol	2-Propanone	Ethyl acetate
in water (experimental)	$11.5 \pm 0.9^*$	9.8 ± 0.9	636 ± 40	7.7 ± 0.3	77 ± 3
ASOG	10.7	5.4	205.0	8.0	81.1
$\left[\frac{\text{ASOG} - \text{exp}}{\text{exp}} \right] \%$	- 7.0	- 45.0	- 68.0	+ 4.0	+ 5.3
in PEG 1500 55 %	12.3 ± 0.9	8.1 ± 0.3	101 ± 20	8 ± 0.6	61 ± 3
ASOG	8.9	6.0	102.0	8.3	89.6
ASOG **	9.1	6.1	110.7	8.41	85.7
$\left[\frac{\text{ASOG} - \text{Exp}}{\text{exp}} \right] \%$	- 26.0	- 25.0	+ 10.0	+ 5.0	+ 41.0

*variation coefficient (%)

**calculated with ASOG modified to take terminal hydroxyl groups into account.

Influence of Temperature. The variation of γ^∞ as a function of temperature permitted the determination of the excess partial molar enthalpy of the compound i ($h^{E\infty}$). The slope of the line $\ln \gamma^\infty$ versus $(1/T)$ is $h^{E\infty}/R$ (where R is the perfect gas law constant). γ^∞ of 2-Propanone increased with temperature in pure water and in 30% solutions of PEG 600 (Table 8). $h^{E\infty}$ for 2-Propanone in water and in PEG 600 was negative and decreased with temperature, but this decrease was smaller in the presence of PEG. This means that a mixture of 2-Propanone in water or in an aqueous solution of PEG is exothermic and the interactions between 2-Propanone and the mixture are weaker than between 2-Propanone and pure water, except for 298.15 K.

Table 8. γ^∞ and $h^{E\infty}$ values of 2-Propanone in water and PEG 600, for solutions at different temperatures

Temperature (K):		298.15	308.15	318.15	328.15
Water	γ^∞	7.7 ± 0.3	8.4 ± 0.2	9.7 ± 0.5	12.6 ± 0.4
	$h^{E\infty}$ (KJ/g mole)	- 3.7	- 9.1	- 15.6	- 28.3
PEG 600 30 % (m/m)	γ^∞	8.7 ± 0.2	9.0 ± 0.2	9.5 ± 0.5	10.6 ± 0.5
	$h^{E\infty}$ (KJ/g mole)	- 5.5	- 5.7	- 5.8	- 6.5

CONCLUSION

By using the technique of exponential dilution adapted for problems encountered with specific foods (high viscosity and foaming) measurements of γ^∞ for volatiles in aqueous mixtures of PEG and measurements of the water activity of these solutions, were made simultaneously.

The repeatability varied between 1 and 2% but the precision for water activity was the same as that with the Lufft technique.

γ^∞ values for volatiles did not vary with the molar mass of PEG but varied with the mole fraction of these compounds in water. Using the ASOG predictive thermodynamic model, the same type of activity coefficient behavior was found for water and for aroma in response to changes in PEG concentrations, but for PEG with molecular weight below 1000 it was necessary to take into account the hydroxyl terminal which induced interactions.

The experimental values of γ^∞ for volatiles showed the importance of entropic phenomena to explain the variation of the activity coefficient with the molecular size of these organic compounds in water.

ACKNOWLEDGMENTS

We thank Professor H. G. Schwartzberg (University of Massachusetts, Amherst, Massachusetts, USA), Professor D. Simatos (ENS.BANA, University of Dijon, France) and Doctor R. Richon (Ecole des Mines, Paris, France) for their interest in this work.

REFERENCES

- ALLANEAU, B. 1979. Influence des lipides sur la retention des constituants volatils. These ENSIA, Massy.
- BUTTERY R. G., LING L. C. and GUADAGNI, D. G. 1969. Volatilities of aldehydes, ketones and esters in dilute water solution. *J. Agr. Food Chem.* 17 (2), 385-389.
- BUTTERY, R. G., BOMBEN, J. L., GUADAGNI, D. G. and LING, L. C. 1971. Some considerations of the volatiles of organic flavor compounds in foods. *J. Agr. Food Chem.* 19 (6), 1045-1048.
- CHANDRASEKARAN, S. K. and KING, C. J. 1972. Cited by KING, C. J. 1983. Physical and chemical properties governing volatilization of flavor and aroma components In *Physical Properties of Foods*. pp. 399-421. I. F. T. Chicago.

- CHIRIFE, J. and FERRO FONTAN, C. 1980. A study of the water activity lowering behavior of polyethylene glycols in the intermediate moisture range. *J. Food Sci.* **45**, 1717-1719.
- DERR, E. L. and DEAL, C. H. 1969. Analytical solutions of Groups: correlation of Activity Coefficients through Structural Group Parameters. I. *Chem. E., Symposium Series*, **32**, 40-51.
- HACHENBERG, H. and SCHMIDT, A. P. 1976. *Gas Chromatographic Headspace Analysis*. Heyden, London.
- KOJIMA, K. and TOCHIGI, K. 1979. *Prediction of Vapor-liquid Equilibria by the ASOG Method*. Elsevier, New York.
- LEBERT, A. and RICHON, D. 1984a. Infinite dilution activity coefficients of n-alcohols as a function of carbohydrates concentration in water-carbohydrates systems. *J. Agri. Food Chem.* **32**, 1156-1160.
- LEBERT, A. and RICHON, D. 1984b. Study of influence of solute (in Alcohols and in Alkanes) chain length on their retention by purified olive oil. *J. Food Sci.* **49** (5), 1301-1304.
- LEROI, J. C., MASSON, J. C., RENON, H., FABRIES, J. F. and SANNIER, H. 1977. Accurate measurement of activity coefficients at infinite dilution by inert gas stripping and gas chromatography. *I.E.C. Process Des. Dev.* **16** (1), 139.
- NORRISH, R. S. 1966. An equation for the activity coefficients and equilibrium relative humidities of water in confectionery syrups. *J. Food Techn.* **1**, 25.
- RICHON, D., SORRENTINO, F. and VOILLEY, A. 1984. Infinite dilution activity coefficients by inert gas stripping method: extension to the study of viscous and foaming mixtures. Accepted by I.E.C. *Process Des. Dev.*
- SORRENTINO, F., VOILLEY, A. and RICHON, D. 1986. Activity coefficients of aroma compounds in model food systems. Accepted by AIChE *J.*
- VOILLEY, A., SIMATOS, D. and LONCIN, M. 1977. Gas phase concentration of volatiles in equilibrium with a liquid aqueous phase. *Lebens. Wissen. und Technol.* **10**, 45-49.
- WILSON, G. M. and DEAL, C. H. 1962. Activity coefficients and molecular structure. *I.E.C. Fundam.* **1** (1), 20-23.

THE EFFECTS OF GAS INJECTION ON THE EFFICIENCY OF THERMAL ENERGY UTILIZATION IN SPRAY DRYING¹

D. E. ROMERO-FERRER²

C. H. AMUNDSON^{3,5}

and

C. G. HILL, JR.⁴

*University of Wisconsin
Madison, Wisconsin 53706*

Submitted for Publication April 1, 1985

Accepted for Publication February 3, 1986

ABSTRACT

Factorial experimental designs were used to study the effects of gas injection on the efficiency of thermal energy utilization in evaporation by spray drying. Both the main effect and the interactions of this variable with feed pressure, feed concentration, nozzle size, and drying temperature were investigated. The use of gas injection led to a decrease in the thermal energy required for evaporation. The magnitude of this effect was larger at the lower levels of feed pressure, feed concentration, and drying temperature. However, this does not imply that spray drying is more energy efficient than such alternative modes of water removal as multi-effect evaporation and reverse osmosis.

¹This paper has been prepared for publication in the *Journal of Food Process Engineering*

²Department of Food Science.

³Departments of Food Science & Agricultural Engineering.

⁴Department of Chemical Engineering.

⁵Direct correspondence to Dr. C. H. Amundson, Department of Food Science, University of Wisconsin, 1605 Linden Drive, Madison, Wisconsin 53706.

INTRODUCTION

Spray drying is the dominant means of converting fluid feedstocks into solids in the form of powders, granules, or agglomerates. It is widely used for purposes of dehydration in the manufacture of a wide variety of food, pharmaceutical, and chemical products. Among the foods that have been successfully spray dried are milk, whey, cheese, coffee, coffee whitener, eggs, soups, baby foods, and fruits. Spray drying has achieved widespread acceptance within the food industry because it is a gentle drying method for heat labile materials and because it lends itself readily to large scale production.

The objective of spray drying is to obtain a product with the desired sensory, functional, and nutritional properties at low cost. Energy costs constitute a significant fraction of the operating costs. Hence a number of methods have been suggested to decrease energy related costs during the spray drying process. As obvious examples one might cite the use of insulation to decrease heat losses to the environment and heat recovery from exhaust gases (e.g., by use of heat exchangers to preheat the feed liquor and/or the inlet air to the dryer).

When gases or sources of gases are introduced in the feedstock prior to atomization, the feed is dried in the form of purposely foamed droplets with the foam being formed either before, during, or after atomization and before or during the drying itself. Hence the term foam spray drying has frequently been used to refer to this technique. The presence of these gases has been reported to influence directly the drying characteristics of the drops, the properties of the dried particles, and the operation of the dryer itself.

It was the purpose of the present study to investigate the effects of gas injection on the efficiency of thermal energy utilization in spray drying. Fractional factorial experimental designs were employed to determine both the main effect and the interactions of gas injection with feed pressure, feed concentration, nozzle size, and drying temperature. The response variable was taken as the total thermal energy input per unit mass of water evaporated. A decrease in the response variable corresponds to an increase in efficiency.

It has long been recognized that the technique of gas injection can be a useful variation on the basic spray drying process. In 1922 Heath and Washburn spray dried milk into which CO_2 had been dissolved under pressure. In more recent years various researchers have utilized gas injection to enhance the physical and sensory properties of the spray dried product (Berlin and Pallansch 1963; Chase and Laursen 1956; Hanrahan *et al.* 1962; Marshall and Seltzer 1950; Reich and Johnston 1957). For example, the use of gas injection leads to products with lower bulk densities than the conventional spray dried product. Reich and Johnston (1957)

have also reported that for coffee and tea extracts, the use of gas injection provides a mechanism for control of the color density of the product. Hanrahan *et al.* (1962) found that gas injection not only leads to a reduction in the moisture content of whole milk powders but also gives enhanced dispersibility/dissolution characteristics. Similar conclusions were reached by Bell *et al.* (1963) in their study of the dispersibility of a spray dried nonfat dry milk product produced using a gas-injection technique. Hanrahan and Webb (1961) have indicated that the use of air injection in drying cottage cheese whey facilitates the drying process by yielding an improved product which does not tend to agglomerate and clog the dryer. Bradley and Stine (1964) have indicated that the use of foam spray drying to produce cheddar cheese powders gives a product with improved flavor quality, larger particle size, and improved shelf-life. They attributed the flavor quality improvement to better retention of flavor volatiles, pointing out that foam spray drying produces a particle with a larger surface area than the conventional process. Apparently the increase in relative surface area facilitates more rapid evaporation of water during dehydration. The higher rate of evaporation produces a more pronounced cooling effect; hence the particles are subjected to less thermal degradation than in the conventional case.

In a study of the effects of dissolved and dispersed gases on the drying of single macrodrops of sodium caseinate, Abdul-Rahman *et al.* (1971) reported enhanced product quality for products dried as foams. They concluded that this improvement resulted from a reduction in the required time for drying. Improvement of product quality apparently was a result of less thermal degradation with little or no change in the evaporative losses of volatile constituents under drying conditions identical to those used in conventional spraying drying. These authors also reported an increased rate of drying for drops of equal mass when compared to nonfoamed drops.

If the injection of gas into the feed liquor produces an increase in the drying rate, the use of gas injection may either accomplish the same amount of evaporation in less time than required for conventional operation, or it may permit the use of milder drying conditions over the same time period. Both approaches result in a reduction in the amount of energy consumed in the evaporation process. It was the purpose of this study to determine the effect of gas injection on the efficiency of thermal energy utilization in spray drying.

MATERIALS AND METHODS

Spray Dryer

A schematic diagram of the University of Wisconsin experimental spray dryer used in this study is shown in Fig. 1. The dryer is 15.54 m high,

the main body of the tower is 2.44 m in diameter, and the drying chamber has a net volume of 51.59 m³. This apparatus has been described in detail by Amundson (1967).

The air is moved through the dryer by means of a single exhaust fan. The fan is powered by a 37,285 w (50 hp) 2-speed motor which was operated at 900 rpm.

The air enters the dryer through louvers which open and close automatically as the fan motor is started or stopped. After passing the louvers, the air moves through a filter and then to the heating units. In the present study only the direct gas-fired heating unit was employed. After leaving the heating unit, the air is sent to two separate ducts in amounts controlled by splitter dampers located at the entrance of each duct.

From the two ducts, the air is directed into the plenum chamber. The air from the upper duct is fed to the central compartment of the plenum chamber where it flows downward through a perforated plate designed to minimize turbulence and create straight line flow into the drying chamber. The air from the lower duct flows into the outer compartment of the plenum chamber where it also is directed downward through a perforated plate into the drying chamber. The two air masses then move together in direct contact.

After leaving the plenum chamber, the air mixes with the product being atomized into the drying chamber and flows downward. At the base of the drying chamber the diameter expands from 2.44 to 3.35 m. The expansion of the air into this larger area slows its velocity sufficiently to permit the major portion of the product to drop out of the air stream and be removed through an air tight rotary release valve. The air containing entrained dust reverses its flow and moves through the exhaust duct system to the cyclonic collectors, where the dust is removed.

A 6-point automatic recording pyrometer equipped with copper-constantan thermocouples was used to measure and record air temperatures at the following locations:

- (1) Downstream from the gas burner,
- (2) In the upper duct,
- (3) In the lower duct,
- (4) In the drying chamber just below the plenum chamber,
- (5) In the drying chamber near the product outlet, and
- (6) In the exhaust duct just before the air is discharged to the atmosphere.

The temperature of the air leaving the gas-fired heating unit was measured using an electronic pyrometer since this temperature exceeded, in most instances, the upper limit which could be measured with the 6-point pyrometer.

The volumetric flow rate of the air was determined by measuring the pressure drop across a constriction in the air duct. A high pressure (68.95

MPa) positive displacement pump was used to supply feed to pneumatic pressure nozzles inserted through the top of the dryer. When gas injection was employed, air was fed from a Corblin, 2 stage diaphragm compressor to the high pressure feed line. Dry and wet bulb temperatures of the ambient air were determined using a hygrometer.

Feedstock

Aqueous solutions of sodium sulfate with solids concentrations ranging from 6.85% to 15% (w/w) were used as the feedstock. This solute was employed because it is not susceptible to damage by either heat or shear forces. Moreover, it is nontoxic, cheap, and is readily soluble in water so as to facilitate cleaning the apparatus.

Experimental Procedure

Within the statistical experimental design each run was carried out as follows:

- (1) Feed liquor of the desired composition was prepared. Samples were taken and stored for subsequent analysis for total solids by the Mojonnier method (Newlander and Atherton 1977).

- (2) The flow of heated air through the spray dryer was initiated and the independent process variables were fixed at the specified levels. The dryer was run until steady state conditions were achieved. Flow of the feed liquor was then initiated.

- (3) The dry and wet bulb temperatures of the incoming air, the pressure drop at the venturi meter and the temperatures of the drying air before and after the heating units, at the inlet plate, and at the bottom and exit of the dryer were recorded.

- (4) After 30 min of operation, the dryer was shut down and the product powder collected from the bottom of the dryer and the cyclones.

- (5) The powder was stored in sealed, plastic bags until it could be analyzed for moisture content by the Toluene Distillation Method (Joslyn 1970).

- (6) Material and energy balances were used to determine the specific energy requirements and the thermal efficiency of the dryer. In performing these calculations, it is important to recognize that the enthalpy of the gas stream is a function of both its temperature and its composition (i.e., its absolute humidity, the mass ratio of the water to the noncondensable gas). Details of such calculations are discussed in conventional textbooks (e.g., Foust *et al.* (1980), and Treybal (1968) and handbooks (Perry and Green 1984).

Four experimental runs were replicated in order to obtain an estimate of the standard deviation of an observation. This in turn was used to estimate the standard error of an effect.

EXPERIMENTAL DESIGNS

The experimental program consisted of three components:

(1) A 2^3 factorial design to determine the effects of three variables (feed pressure, nozzle size, and the presence or absence of gas injection) on the thermal energy utilized to evaporate a unit mass of water.

(2) A 2^4 factorial design to study the effects of four variables (feed concentration, drying temperature, feed pressure, and the presence or absence of gas injection) on said energy.

(3) Studies of interactions between the gas-injection variables and other variables that were determined to be significant in the aforementioned factorial design experiments. These were the interactions of gas injection (presence or absence) and feed pressure, feed concentration, and drying temperature.

The results were analyzed using standard statistical procedures for factorial experimental designs (Box *et al.* 1978).

Each of the aforementioned components is discussed in more detail below.

The 2^3 Factorial Design

Since it was impossible to carry out eight experimental runs in a single day and since the environmental conditions (e.g., the temperature and humidity of the air) were expected to vary from day to day, the 2^3 factorial design experiments were blocked by day, i.e., they were run in two blocks of four runs each; each block representing a day. The block variable was confounded with the three-factor interaction. The experimental design used is presented in Table 1.

In addition, on a given day the runs were carried out in random order as follows:

First day: 1, 6, 4, and 7.

Second day: 3, 8, 2, and 5.

The 2^4 Factorial Design

The analysis of the results of the 2^3 factorial design experiments indicated that the feed pressure had a large effect on the thermal energy utilized for evaporation and a significant interaction with gas injection. For this reason, it was included again in this design, this time with an expanded range. On the other hand, the nozzle size did not show, at least in the range studied, a significant interaction with gas injection. Hence, it was held constant in this second sequence of experiments.

The experiments in the 2^4 design were also blocked by day. The block variables were confounded with the pressure-feed concentration-gas injection, feed concentration-gas injection-drying temperature, and feed

Table 1. 2^3 factorial design

In all experiments:

Feed Concentration = 7.6% w/w

Drying Temperature = 157.2°C

Experimental Variables					Block Variable				
Run	P	N	G	B = PNG	Block	P	N	G	Run
1	-	-	-	-	I	-	-	-	1
2	+	-	-	+		+	+	-	4
3	-	+	-	+		+	-	+	6
4	+	+	-	-		-	+	+	7
5	-	-	+	+	II	+	-	-	2
6	+	-	+	-		-	+	-	3
7	-	+	+	-		-	-	+	5
8	+	+	+	+		+	+	+	8

Levels of the Variables

Level	Feed Pressure (P) (MPa)	Nozzle Orifice Diameter (N) (cm)	Gas Injection (G)
-	6.89	0.079	Without
+	13.79	0.107	With

pressure-drying temperature interactions, respectively. The experimental design used is presented in Table 2.

The experimental runs were carried out in random order as follows:

First day: 1, 14, 7, 12

Second day: 9, 6, 15, 4

Third day: 13, 2, 11, 8

Fourth day: 5, 10, 3, 16

Studies of Interaction Effects

This component of the research focused on those interaction effects of gas injection and other process variables that the 2^3 and 2^4 factorial designs indicated were significant.

Table 2. 2⁴ factorial design

In all experiments: nozzle orifice diameter = 0.079 cm

Run	Experimental Variables				Block Variables			Block	P	C	G	T	Run
	P	C	G	T	B1=PCG	B2=CGT	B1B2=PT						
1	-	-	-	-	-	-	+	1	-	-	-	-	1
2	+	-	-	-	+	-	-		-	+	+	-	7
3	-	+	-	-	+	+	+		+	+	-	+	12
4	+	+	-	-	-	+	-		+	-	+	+	14
5	-	-	+	-	+	+	+	2	+	+	-	-	4
6	+	-	+	-	-	+	-		+	-	+	-	6
7	-	+	+	-	-	-	+		-	-	-	+	9
8	+	+	+	-	+	-	-		-	+	+	+	15
9	-	-	-	+	-	+	-	3	+	-	-	-	2
10	+	-	-	+	+	+	+		+	+	+	-	8
11	-	+	-	+	+	-	-		-	+	-	+	11
12	+	+	-	+	-	-	+		-	-	+	+	13
13	-	-	+	+	+	-	-	4	-	+	-	-	3
14	+	-	+	+	-	-	+		-	-	+	-	5
15	-	+	+	+	-	+	-		+	-	-	+	10
16	+	+	+	+	+	+	+		+	+	+	+	16

Levels of Variables

Level	Pressure (P) (MPa)	Feed Concentration (C) (w/w%)	Gas Injection (G)	Drying Temperature (°C)
-	6.89	7.5	With	204.44
+	20.68	15.0	Without	148.89

Feed Pressure-Gas Injection (PG) Interaction. In this set of experiments, the feed concentration was fixed at 6.85 w/w%, the drying temperature at 165.56°C and the nozzle size at 0.079 cm orifice diameter. Ten experimental runs were carried out. The amount of thermal energy utilized

for evaporation was estimated with and without gas injection at each of the following feed pressures: 6.89, 10.34, 13.79, 17.24, and 20.68 MPa.

Feed Concentration-Gas Injection (CG) Interaction. In this group of experiments the feed pressure was fixed at 6.89 MPa, the nozzle size at 0.079 cm orifice diameter, and the drying temperature at 162.78 °C. Eight experimental runs were carried out. The amount of thermal energy used for evaporation was estimated with and without gas injection at each of the following feed concentrations: 7.5, 10.0, 12.5, and 15.0 w/w%.

Drying Temperature-Gas Injection (TG) Interaction. In this set of experiments, the feed pressure was fixed at 6.89 MPa, the feed concentration at 7.6 w/w%, and the nozzle size at 0.079 cm orifice diameter. Eight experimental runs were carried out. The amount of thermal energy needed for evaporation was estimated with and without gas injection at each of the following drying temperatures: 160, 190.56, 207.22, and 229.44 °C.

RESULTS AND DISCUSSION

The 2³ Factorial Design

The results of this design are summarized in Table 3. The response variable is the total quantity of thermal energy supplied by the air stream

Table 3. Calculated effects and standard errors for the 2³ factorial design

Effect	Estimate of Response Variable ± Standard Error*
	kJ/Kg H ₂ O
Average	(15984 - q _L **) ± 56
Main Effects	
Feed Pressure, P	-5897 ± 112
Nozzle Size, N	-5729 ± 112
Gas Injection, G	-749 ± 112
Two-Factor Interactions	
P × N	1250 ± 112
P × G	409 ± 112
N × G	128 ± 112***
Three-Factor Interaction	
P × N × G	-13 ± 112***

*with 4 degrees of freedom

**q_L represents the thermal energy losses from the dryer per unit mass of water evaporated

***not significant

per unit mass of water evaporated. Note that the average of the response variable is inflated by a term involving q_L , the thermal energy losses from the dryer per unit mass of water evaporated. In the present study, we were not interested in the absolute values of the response variable but in how this variable changes on going from the lower to the higher level of each independent variable. Since neither the environmental conditions nor the operating conditions of the spray dryer changed dramatically from run to run and since the effect of each independent variable is computed as the difference between the averages of the response variable at the high and low values of the independent variables, the q_L term effectively cancels out of the calculations and any small variations in q_L become buried in the estimate of the standard error.

It should also be noted that the method of analysis used in this study did not encompass the component of overall process energy requirements associated with compression of the injected gas. Such a study is currently in progress.

The results in Table 3 indicate that all the main effects and the interaction effects PN and PG are significant. This conclusion is discussed in more detail below.

An increase in feed pressure from 6.89 to 13.79 MPa or an increase in nozzle orifice diameter from 0.079 to 0.107 cm significantly decreases the amount of thermal energy used for evaporation. However, due to the large interaction between these two variables, they cannot be analyzed individually. Their joint effect can be analyzed according to the two-way table below where the numbers at the corners represent the values of the response variable at the conditions in question and where the values on the sides of the rectangle correspond to differences in the values of the response variable.

			(-4478)	
(+)	(15274)	—————	(10796)	
P				(-4646)
		(-7147)		
(-)	(22421)	—————	(15442)	
		(-6979)		
	(-)	N	(+)	

From the two-way table it is evident that:

- (1) The effect of nozzle size is larger at the lower feed pressure.
- (2) The effect of feed pressure is larger at the smaller nozzle size.

The results obtained for the effects of feed pressure and nozzle size on the energy used for evaporation are susceptible to obvious interpretation.

An increase in feed pressure or nozzle size produces an increase in the liquid feed rate leading to a concomitant decrease in the energy requirement per unit mass of water evaporated. As long as the feed rate lies below that which would render it impossible to produce a dry solid product, the increase in the flow rate leads to an increase in the efficiency of energy utilization. The effect of pressure is larger at the smaller nozzle size because a smaller nozzle orifice produces a finer spray with a concomitant increase in the surface area across which heat and mass can be transferred. The greater effect of nozzle size at the lower feed pressure can also be explained in terms of a concomitant increase in interfacial surface area.

The use of gas injection also produces a decrease in the energy used for evaporation, the magnitude of the effect depending upon the level of feed pressure. The extent of the PG interaction is illustrated in Fig. 2. At a feed pressure of 6.89 MPa the use of gas injection produces a decrease of 1158 kJ/Kg H₂O in the energy used for evaporation compared to a decrease of 341 kJ/Kg H₂O at a feed pressure of 13.79 MPa. The use of gas injection produces a decrease in the energy used for evaporation due to the increase in surface area that results from the expansion of the injected gas within the droplets upon release of the pressure at the exit of the nozzle orifice. As noted above, a larger surface area results in larger heat and mass transfer rates. The effect of gas injection is larger at the lower feed pressure because the lower the feed pressure, the greater the range of particle sizes produced and the larger the average particle diameter. Since drying rates are proportional to the square of the particle diameter, gas injection is more effective in increasing the interfacial surface area at low pressures.

The NG interaction was not statistically significant.

The 2⁴ Factorial Design

The results of this design are summarized in Table 4. The comments noted above concerning the average of the response variable are again applicable to the present analysis. The results in Table 4 indicate that all the main effects, five of the two-factor interactions (all except CT), and the PGT three-factor interaction are significant. The main effects and the interactions of gas injection with the other variables are discussed below.

The results obtained for the effects of feed pressure and gas injection on the energy used for evaporation are very similar to those obtained in the 2³ factorial design. The magnitudes of the effects are somewhat different but the conclusions are the same. The differences in magnitude are due (a) to the expansion of the feed pressure range and (b) to the inclusion of new variables (feed concentration and drying temperature) which interact significantly with the feed pressure and gas injection. The PG interac-

Table 4. Calculated effects for the 2^4 factorial design

Effect	Estimate of Response Variable ± Standard Error*
	$\text{kJ/Kg H}_2\text{O}$
Average	$(17699 - q_L^{**}) \pm 43.5$
Main Effects	
Feed Pressure, P	-10043 ± 87
Feed Concentration, C	1034 ± 87
Gas Injection, G	-598 ± 87
Drying Temperature, T	2401 ± 87
Two-Factor Interactions	
P x C	-280 ± 87
P x G	337 ± 87
C x G	369 ± 87
P x T	-892 ± 87
C x T	$175 \pm 87^{***}$
G x T	278 ± 87
Three-Factor Interaction	
P x C x G	$41 \pm 87^{***}$
P x C x T	$-164 \pm 87^{***}$
C x G x T	$-130 \pm 87^{***}$
P x G x T	-411 ± 87
Four-Factor Interaction	
P x C x G x T	$171 \pm 87^{***}$

*with 4 degrees of freedom

** q_L represents the thermal energy losses from the dryer per unit mass of water evaporated

***not significant

tion effect was very similar in magnitude and direction to that obtained in the 2^3 factorial design.

An increase in feed concentration produces an increase in the thermal energy used for evaporation, the magnitude of the effect depending on the feed pressure level. The extent of the PC interaction is illustrated in the following two-way table.

		(755)	
(+)	(12300)	—————	(13055)
P		(-9763)	
			(-10322)
(-)	(22063)	—————	(23377)
		(1314)	
	(-)	C	(+)

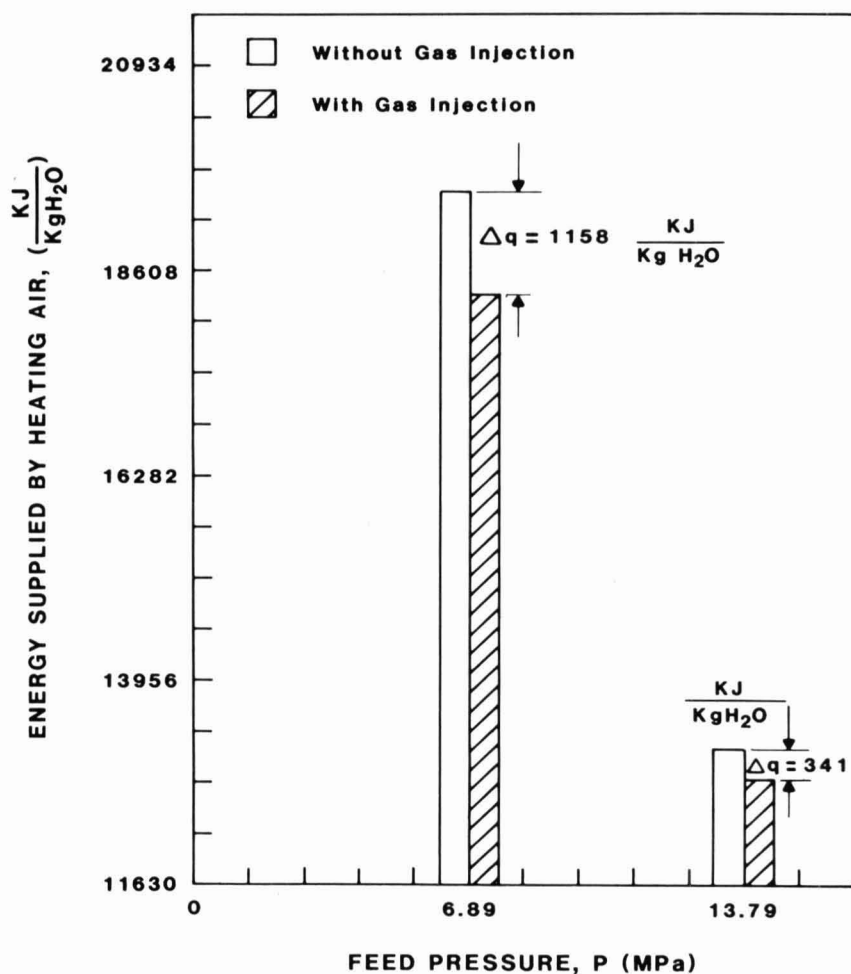


FIG. 2. FEED PRESSURE-GAS INJECTION (PG) INTERACTION
 [DRYING TEMPERATURE = 166°C; ORIFICE DIAMETER = 0.079 cm;
 FEED CONCENTRATION = 6.85% (w/w)]

As the above table indicates, the effect of concentration is larger at the lower feed pressure. This result may be attributed to the fact that at a higher feed pressure the feed temperature increases gradually as drying proceeds, producing a concomitant decrease in feed viscosity. This temperature rise has its origins in viscous dissipation caused by recirculation of a portion of the feed through the bypass loop. The lower the viscosity, the finer the spray, the higher the dryer rate, and the lower the effect of increasing the feed concentration on the energy used for evaporation. The effect of feed concentration itself can be attributed to the associated increase in feed

viscosity. Moreover, as the feed concentration increases, there is a decrease in liquid feed flow rate necessary to produce a unit of solid product. Hence, there is a concomitant increase in the amount of thermal energy used to evaporate a unit quantity of water. Viewed from another perspective, at constant feed rate there is a greater quantity of solids produced at the higher feed concentration. Per unit of product less energy will then be required.

The feed concentration interacts significantly with gas injection. The magnitude of the interaction is illustrated in Fig. 3. The effect of gas injection is larger at the lower feed concentration. At 7.5% w/w solids content, the use of gas injection causes a decrease of 967 kJ/Kg in the energy used for evaporation; at 15% w/w solids content, the decrease is only 229 kJ/Kg H_2O .

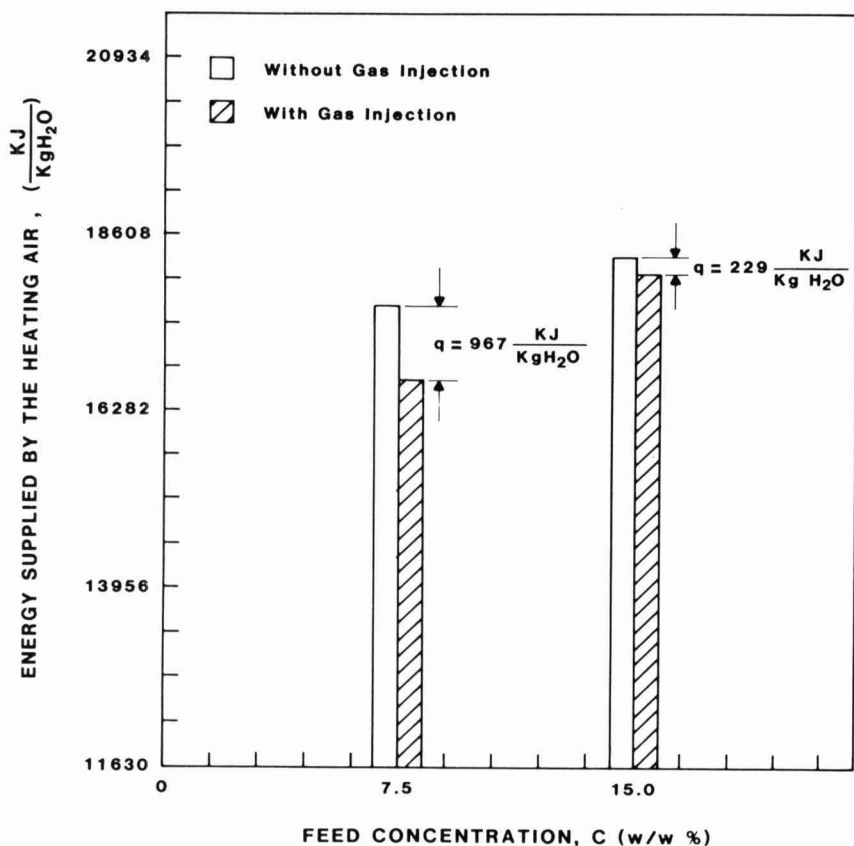


FIG. 3. FEED CONCENTRATION-GAS INJECTION (CG) INTERACTION
 [FEED PRESSURE = 6.89 MPa; ORIFICE DIAMETER = 0.079 cm;
 DRYING TEMPERATURE = 163°C]

The larger effect of gas injection at the lower feed concentration can be attributed to factors associated with the viscosity of the liquid feed. At the lower solute concentration, the fluid viscosity is lower; hence, the resultant spray droplets are smaller and have a larger total surface area, thereby facilitating the drying process. At the high solute concentration, the fluid viscosity is higher and the expansion of the injected gas within the liquid is more restricted, resulting in a lower effect of gas injection.

An increase in the drying temperature produces an increase in the thermal energy used for evaporation. This result may be attributed to a combination of factors. The enhanced driving force used to effect the drying process not only produces higher energy losses to the environment but also can cause increased mechanical resistance to expansion (Crosby and Weyl 1976).

The effect of gas injection on the efficiency of thermal energy utilization is significantly influenced by the drying temperature employed. As Fig. 4 indicates, the effect of gas injection is larger at the lower drying temperature. At a drying temperature of 149 °C, the use of gas injection produces a decrease of 876 kJ/Kg in the energy used for evaporation. At a drying temperature of 204 °C, the decrease is only 319 kJ/Kg. This result was not anticipated because one would expect the expansion of the gas within the droplet to be greater at a higher drying temperature. However, as Crosby and Weyl (1976) have noted, when the drying temperature increases, the drop dries faster and develops mechanical resistance to expansion much sooner. Thus, as the drying temperature increases, there is less expansion of the gas and the effect of gas injection is reduced.

Studies of Interaction Effects

Feed Pressure-Gas Injection Interaction (PG). The results obtained in the PG interaction study are summarized in Fig. 5. As the feed pressure increases, the effect of gas injection on the thermal energy used for evaporation decreases. The data corroborate the results obtained in the factorial design experiments. The use of gas injection caused a larger decrease in process energy requirements at lower feed pressures because of the reasons noted.

Feed Concentration-Gas Injection Interaction (CG). Figure 6 depicts the results obtained in the CG interaction study. At the lower feed concentrations gas injection produces greater reductions in evaporation energy requirements. These results confirm the conclusions drawn from the factorial design experiments and can be explained as noted above.

Drying Temperature-Gas Injection Interaction (TG). The results obtained in the TG interaction study are summarized in Fig. 7. The effect

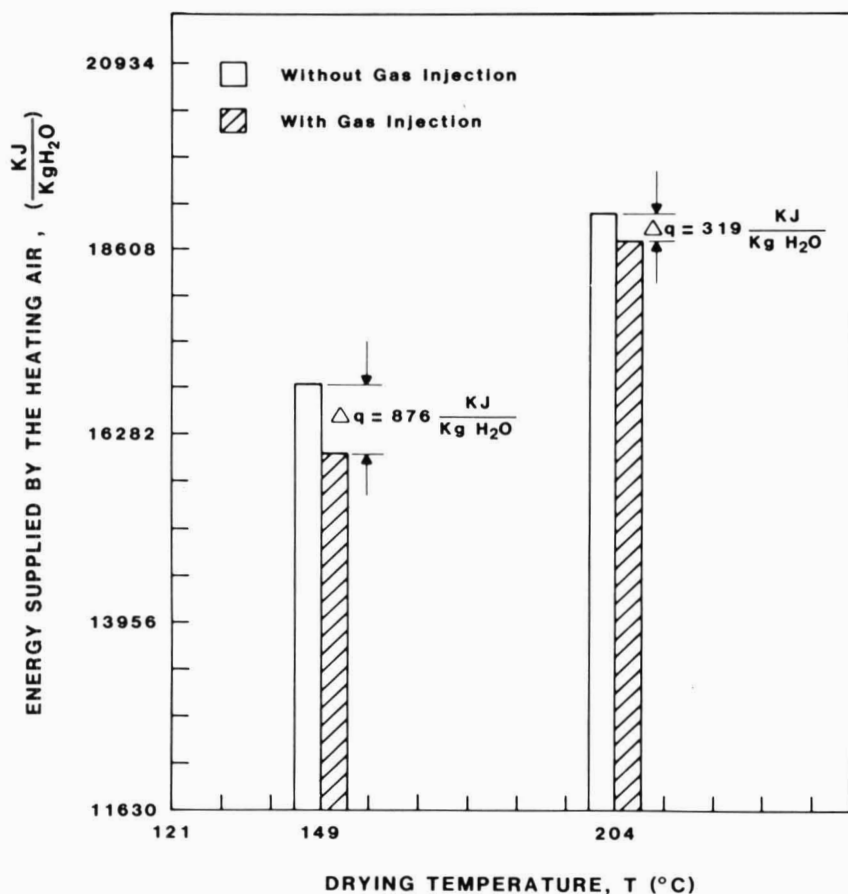


FIG. 4. DRYING TEMPERATURE-GAS INJECTION (TG) INTERACTION
 [FEED PRESSURE = 6.89 MPa; FEED CONCENTRATION = 7.6% (w/w);
 ORIFICE DIAMETER = 0.079 CM]

of gas injection on the thermal energy used for evaporation is larger at the lower drying temperature. As noted in the discussion of the results of the 2^4 factorial design experiments, this effect can be explained by the fact that as the drying temperature increases, the droplets dry faster and more rapidly develop mechanical resistance to the expansion of the gas within the droplet.

CONCLUSIONS

The results of this study indicate that the use of gas injection produces a significant decrease in thermal energy requirements for spray drying.

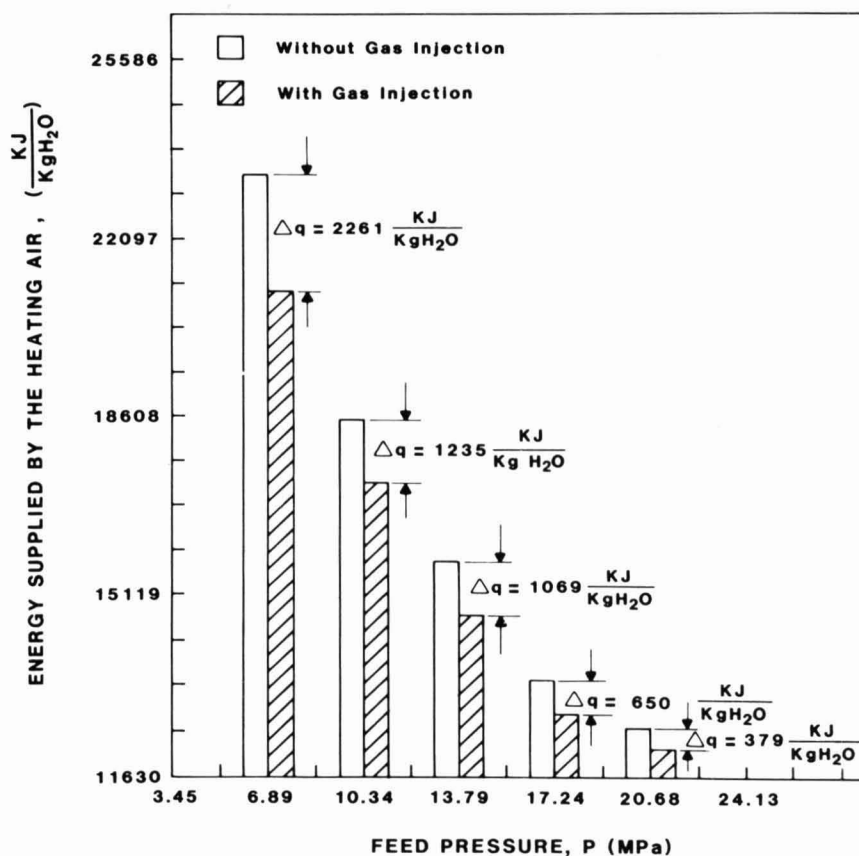


FIG. 5. INFLUENCE OF FEED PRESSURE ON THE EFFECT OF GAS INJECTION ON THE THERMAL ENERGY USED FOR EVAPORATION

The magnitude of this effect depends on the levels of such other variables as feed pressure, feed concentration, and drying temperature. Gas injection produces the largest reductions in evaporation energy requirements at the lower level of each of the above-mentioned variables. However, this does not imply that spray drying is more energy efficient than such alternative processes as multi-effect evaporation and reverse osmosis.

ACKNOWLEDGMENTS

This work was supported in part by the Food Engineering Pilot Plant, the College of Agricultural and Life Sciences, University of Wisconsin-Madison, and the Stauffer Chemical Company. The authors also wish to thank Horst Gierke for assistance in the operation and maintenance of Pilot Plant equipment.

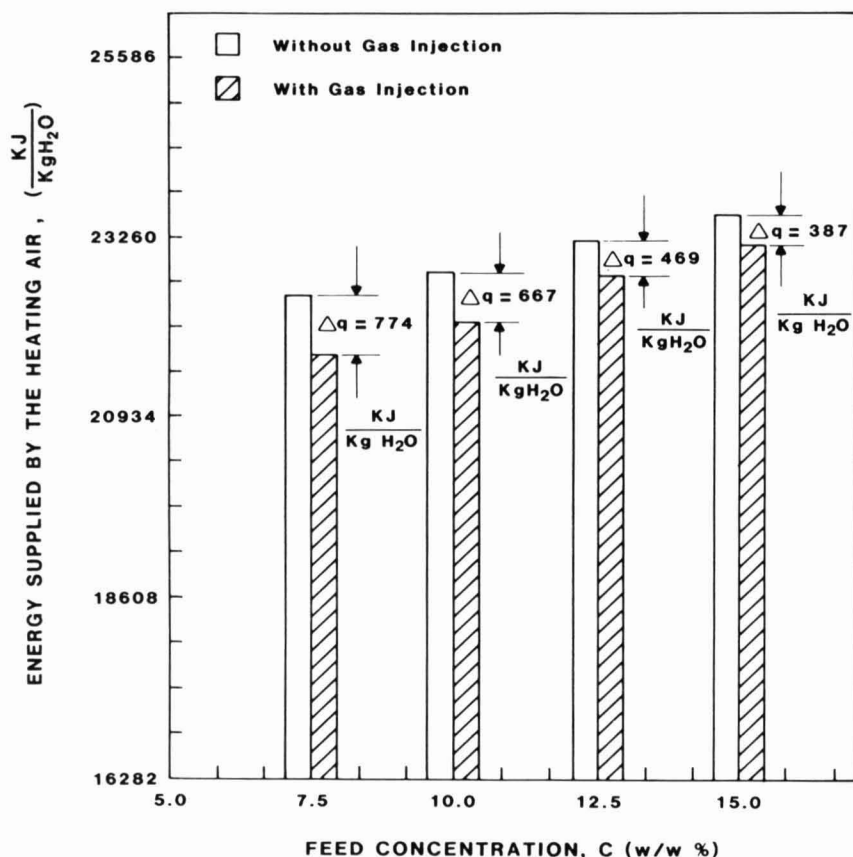


FIG. 6. INFLUENCE OF FEED CONCENTRATION ON THE EFFECT OF GAS INJECTION ON THE THERMAL ENERGY USED FOR EVAPORATION

REFERENCES

- ABDUL-RAHMAN, Y. A. K., CROSBY, E. J. and BRADLEY, R. L., JR. 1971. Drying of single drops of foamed and nonfoamed sodium caseinate solutions. *J. Dairy Sci.* **54** (8), 1111-1118.
- AMUNDSON, C. H. 1967. Spray drying dairy and food products. *ASHRAE* **9** (3), 70-73.
- BELL, R. W., HANRAHAN, F. P. and WEBB, B. H. 1963. Foam spray drying methods of making readily dispersible nonfat dry milk. *J. Dairy Sci.* **46** (12), 1352-1356.
- BERLIN, E. and PALLANSCH, M. J. 1963. Influence of drying methods on density and porosity of milk powder granules. *J. Dairy Sci.* **46** (8), 780-784.

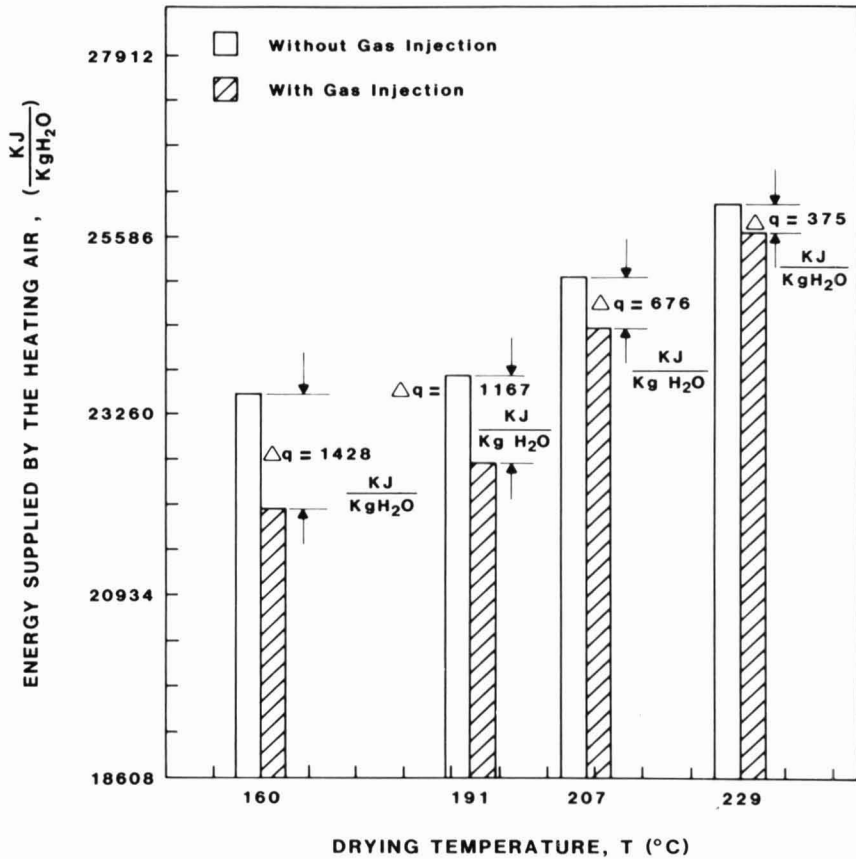


FIG. 7. INFLUENCE OF DRYING TEMPERATURE ON THE EFFECT OF GAS INJECTION ON THE THERMAL ENERGY USED FOR EVAPORATION

- BRADLEY, R. L., JR. and STINE, C. M. 1964. Foam spray drying of natural cheese. *Mfg. Milk Prod. J.* 55 (6), 8-11.
- BOX, G. E. P., HUNTER, W. G. and HUNTER, J. S. 1978. *Statistics for Experimenters*, John Wiley & Sons, New York.
- CHASE, F. A. and LAURSEN, G. E. 1956. Carbonation of coffee extract. U.S. Patent 2,771,364.
- CROSBY, E. J. and WEYL, R. W. 1976. Foam spray drying: general principles. *AIChE Symposium Series*, 73 (163), 82-94.
- FOUST, A. S., WENZEL, L. A., CLUMP, C. W., MAUS, L. and ANDERSEN, L. B. 1980. *Principles of Unit Operations*, second edition, chaps. 17 & 18, John Wiley & Sons, New York.
- HANRAHAN, F. P., TAMSMA, A., FOX, K. K. and PALLANSCH, M. J. 1962. Production and properties of spray-dried whole milk foam. *J. Dairy Sci.* 45 (1), 27-31.

- HANRAHAN, F. P. and WEBB, B. H. 1961. USDA develops foam spray drying. *Food Eng.* 33 (8), 37-38.
- HEATH, W. P. and WASHBURN, R. M. 1922. Spray desiccation of milk. U.S. Patent 1,406,381.
- JOSLYN, M. A. 1970. *Methods in Food Analysis*, Academic Press, New York.
- MARSHALL, W. R., JR. and SELTZER, E. 1950. Principles of spray drying. II. Elements of spray-drier design. *Chem. Eng. Prog.* 46 (11), 575-584.
- NEWLANDER, A. J. and ATHERTON, H. V. 1977. *The Chemistry and Testing of Dairy Products*, 4th ed. AVI Publishing Co., Westport, CT.
- PERRY, R. H. and GREEN, D. W. 1984. *Perry's Chemical Engineers' Handbook*, 6th Ed. Sec. 20, McGraw-Hill, New York.
- REICH, I. M. and JOHNSTON, W. R. 1957. Spray drying of foamed materials. U.S. Patent 2,788,276.
- TREYBAL, R. E. 1968. *Mass Transfer Operations*, second edition, chaps. 7 & 12, McGraw Hill, New York.

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CONTENTS

Meetingsv

Effect of Different Tube Materials on the Steady Shear Tube Flow of Semi-Solid Foods
M. DERVISOGLU and J.L. KOKINI 137

Water Absorption in Cereal Grains and Its Effect on Their Rupture Stress
E.U.U. ITUEN, J.P. MITTAL and J.S. ADEOTI 147

Activity Coefficients of Aroma Compounds and Water Activity in Model Systems
A. VOILLEY 159

The Effects of Gas Injection on the Efficiency of Thermal Energy Utilization in Spray Drying
D.E. ROMERO-FERRER, C.H. AMUNDSON and
C.G. HILL, JR. 171