Volatiles Loss During Atomization in Spray Drying

Losses of volatile acetates have been measured in the vicinity of pressure nozzles during spraying of sucrose and maltodextrin solutions. Large losses occur very near the atomizer, where only a small portion of the water has evaporated. The effects of atomizer design, nozzle pressure, sucrose concentration, air flow rate, air temperature and liquid feed temperature have all been measured. Correlation of volatiles loss vs. percent water evaporation accounts for most of the effects of changes in spray pattern and drop size distribution. Individual contributions of gas and liquid phase mass transfer are determined from the relative retentions of acetates of different molecular weight and from the effect of sucrose concentration. In the expanding film at the nozzle, both gas and liquid phase resistances are important, but the losses become entirely liquid phase controlled once drops are formed.

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SCOPE

Poor product quality in spray drying of liquid and paste form foods often results from loss of volatile flavor and aroma substances. Previous studies have shown that retention of these substances is promoted by development of a surface layer of high dissolved solids content, which selectively holds back the volatiles. Losses in practice are much less than predicted for equilibrium vaporization but substantially greater than predicted for loss by diffusion from stagnant spheres. Previous measurements of losses near the atomizer for foods and food models are sparse, scattered and contradictory. The purposes of the present work were to ascertain the extent of volatiles loss very near to the atomizer for spraying of sucrose solutions with pressure swirl nozzles, to determine the effects of a number of operating parameters and to interpret the results in terms of fundamental mass transfer mechanisms.

CONCLUSIONS AND SIGNIFICANCE

The principal result is that losses of volatile substances are very large in the immediate vicinity of the nozzle, where only very little water has evaporated. Therefore efforts to reduce volatiles loss for solutions similar to those studied here should be directed at the nozzle zone.

The loss patterns observed can be rationalized, at least qualitatively, through fundamental concepts of diffusional mass transfer. Differences in spray pattern and drop size distribution can be accounted for, in large part, by interpreting volatiles loss as a function of the fraction of the feed evaporated, rather than as a function of distance from the nozzle. The loss appears to be dominated by both gas and liquid phase mass transfer resistances in the expanding film adjacent to the nozzle but becomes liquid phase controlled once drops are formed. Losses are less for higher sucrose concentrations, reflecting lower volatiles diffusion coefficients in the liquid. Losses are also less for maltodextrin solutions of equivalent viscosity than for sucrose solutions. Losses increase with increasing liquid feed temperature, reflecting higher liquid diffusion coefficients and Henry's law constants in the expanding film. Higher air temperatures suppress losses at equivalent degrees of evaporation, substantiating a prediction of the selective-diffusion model.

Spray drying is a convenient and economical technique for dehydration and preservation of foods. However, product quality often suffers from large loss of highly volatile flavor and aroma components (Bomben et al., 1973).

In spray drying, the loss of volatiles is usually much less than would be expected on the basis of equilibrium unsteady state (Rayleigh) vaporization. This indicates a dominant influence of mass transfer resistance. Thijssen and Rulkens (1968) observed a steep decrease of liquid phase diffusion coefficients for volatiles with increasing dissolved solids concentration. On the basis of this result, they formulated the selective-diffusion concept, where higher than equilibrium volatiles retention can be explained by formation of a region of high dissolved solids content near the surfaces of droplets at an early phase of drying. Water can still diffuse through this region, but the movement of volatiles is more severely hindered.

Experimental results reported by Rulkens and Thijssen (1972) sustain this concept. The feed characteristics (dissolved solids concentration, type of volatile species and feed temperature) were the most influential variables, and the retention increased with changes in conditions that would be expected to favor more rapid formation of a surface region of high dissolved solids content. Departures from this trend were attributed to underdeveloped atomization, fissures in the dry crust and/or losses during atomization. Other investigators (Reineccius and Coulter, 1969; Blakebrough and Morgan, 1973) have also emphasized the influence of the dissolved solids concentration of the feed on volatiles retention in spray drying.

Kerkhof and Thijssen (1977) interpreted volatiles loss in spray drying in terms of a diffusion model and observed that losses in actual spray drying were greater than predicted by the model. They attributed the additional loss to the drop formation period

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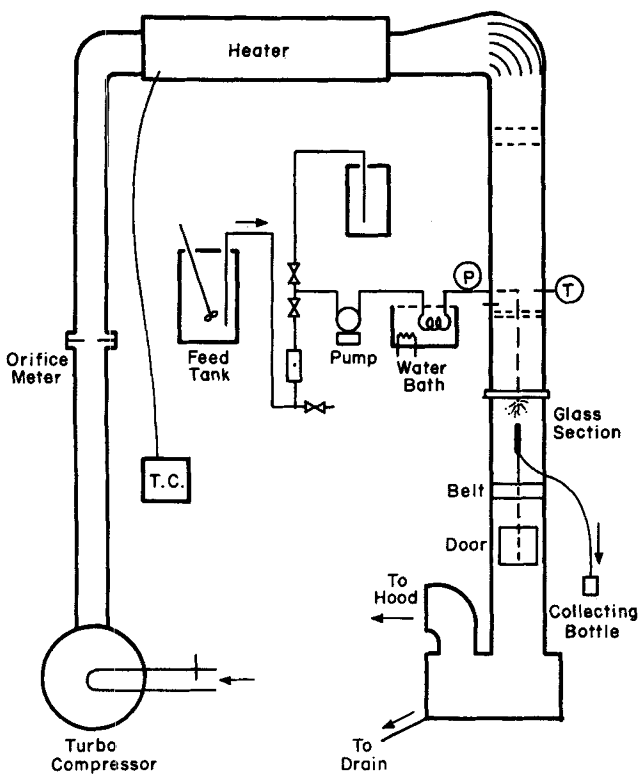

Figure 1. Experimental apparatus.

for low liquid feed concentrations and to cracking in the dry crust at high feed concentrations.

Previous experimental measurements of volatiles losses during atomization are sparse and not conclusive. Rulkens and Thijssen (1972) showed that higher losses occur when the spray is formed before contacting the hot drying air. Rulkens (1973), releasing frozen particles into a spray chamber, concluded that the losses of volatiles from the liquid cone and during drop formation were probably relatively small. Goorden (1974) used liquid nitrogen to catch samples of sprayed maltodextrin solutions at different distances from a pressure nozzle and found about 15% loss of *n*-alcohols in the first 10 cm. For the same system, the retention after full drying was less than 20% (Rulkens, 1973). Goorden found no loss in the first 2 cm and a nearly linear loss with distance, although there was considerable scatter. This was attributable, in part, to lack of reproducibility with the analytical procedure; the evolving nitrogen gases may also have affected the sampling and/or drying behavior.

These measured losses near the nozzle are considerably less than would be expected by extrapolation of data from spray desorption experiments. Simpson and Lynn (1977) report almost complete equilibration at 26 cm from a pressure nozzle in vacuum spray desorption of sparingly soluble gases from aqueous solutions, with most of the equilibration occurring in the film zone, less than 2 cm from the nozzle. Similar results were obtained by Lin et al. (1977).

The present work involved measurements of losses of volatiles and evaporation rates in the vicinity of pressure nozzles during spray drying. Sucrose and maltodextrin solutions were used, with acetates added as volatile components.

EXPERIMENTAL EQUIPMENT AND OPERATING PROCEDURES

The experimental spray drying chamber used in the present investigation was described in detail by Kieckbusch and King (1977). A schematic drawing of the apparatus is given in Figure 1. The section of main interest was a glass chamber, 0.17 m ID and 0.40 m long, where heated air contacted sprayed liquid co-currently. The air supply, measured by a calibrated orifice meter, was heated electrically. The liquid temperature, read by means of a thermocouple placed inside the line just before the nozzle, was controlled through a water bath. The liquid flow rate was monitored with a calibrated rotameter.

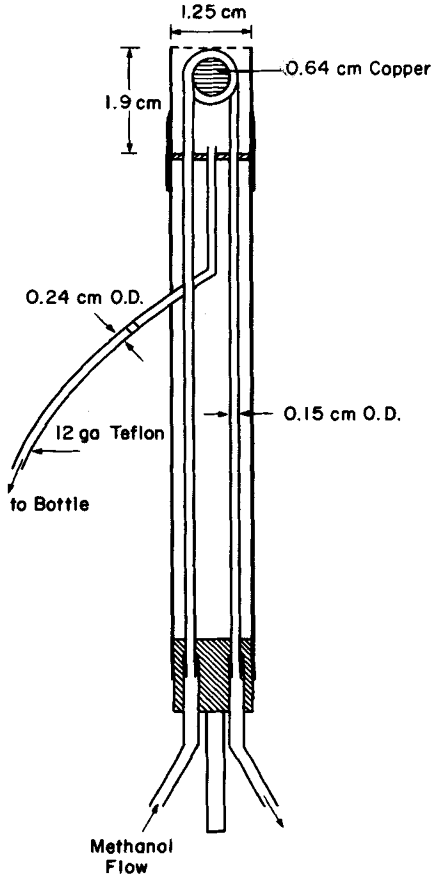

Figure 2. Standard collector.

Spraying Systems Company pressure nozzles were used. Most of the data were taken with Model LN-1, a centrifugal pressure nozzle. Considerable variation in spray cone angle could be obtained by interchanging the orifice inserts.

Spray Collection

The spray was collected by means of a refrigerated probe designed to capture a continual flow of liquid drops while suppressing both additional volatiles loss and additional drying during sampling and minimizing disturbances of the flow pattern as well. The dimensions and characteristics of the standard sampler used are shown in Figure 2. The spray receiving cell was refrigerated by a 12 cm long tube, 0.104 cm ID, coiled around a small copper block. Methanol, cooled in a dry ice-isopropanol bath, was pumped through this tube. The collected liquid was purged through the bottom of the cell.

During operation, the Teflon tube indicated in Figure 2 was passed through one of the ports in the wall of the glass chamber and was connected to one of several enclosed 120 cm^3 sample bottles. The bottles were marked, and 25 mL were collected each time, after sufficient purging of the line.

Provisions were made for positioning the whole sampling cell assembly at 0.5 cm intervals, axially and radially.

Analytical Procedure

The liquid collection bottles were equipped with magnetic stirrer bars and Teflon caps, and were immersed in ice water. A separate sample was drawn for determination of sucrose content by an Abbé refractometer. The amount of evaporation was determined from the increase in sucrose concentration.

Concentrations of the volatile acetates were determined gas chromatographically with a Perkin-Elmer Model 3920 gas chromatograph, using a 0.5 m Porapak Q column. Water was first added in an

TABLE 1. EFFECT OF COLLECTOR TEMPERATURE ON MEASURED RETENTION (20% SUCROSE; 5 CM FROM THE NOZZLE)

Methanol temperature, °K	wt % sucrose	% acetate retention Ethyl	Propyl	Butyl	Pentyl
316	20.86	25.4	23.3	22.1	21.6
250	20.77	37.3	35.4	34.4	33.9
240	20.75	41.2	39.7	38.9	39.1
235	20.73	42.1	40.5	39.7	39.6
229	20.73	42.4	41.0	40.4	40.8
223	20.73	42.7	41.3	40.7	41.1
222	20.73	42.5	41.0	40.3	40.7

amount to return the sample to the original sucrose concentration, and the liquid was left to equilibrate in the closed bottle in a water bath at a temperature of 25°C. Samples of the gas phase were withdrawn by syringe through the Teflon cap and were injected into the chromatograph. The peak areas were compared to the corresponding areas for the feed solution in order to obtain the percent retention. Calibration showed that the response was linear. Reproducibility of consecutive injections was better than 1%. A number of precautions had to be taken because of the low concentrations of volatiles present; these are detailed elsewhere (Kieckbusch and King, 1979*a*).

Standard Conditions

The following conditions were used most often and were denoted as standard conditions:

Liquid feed temperature at the nozzle (T_{LN}): 316°K
Differential nozzle pressure (P): 0.79 MPa (100 lb/in.^{2}gauge)
Air temperature at nozzle level (T_{air}): 433°K
Air flow rate: 100 kg/h
Feed concentrations of acetates: 40 ppm (w/w) each

The standard liquid feed temperature was chosen to correspond closely to the wet bulb temperature of the system. Unless indicated otherwise, all sample collections were made on the center line of the chamber at various distances below the nozzle. When results are shown for several different acetates, all were present simultaneously in a single run.

TESTING OF THE SAMPLER

Since the sampler was crucial to this work, extensive tests were performed in order to estimate its accuracy and reliability. Preliminary results were discussed by Kieckbusch and King (1977).

The predominant factor influencing the behavior of the collector was the amount of cooling provided by the methanol coil. Table 1 reports acetate retentions measured axially 5 cm below the nozzle, during spraying of a 20% sucrose solution. The methanol temperature inside the coil was estimated by measuring the methanol temperature before it entered and after it left the spray chamber, and averaging these values. The sucrose content was measured with a Carl Zeiss (Jena) differential interferometer. The retention increased somewhat with decreasing methanol temperature, but levelled off below approximately 235 K. During a normal drying run, a temperature of about 223 K was maintained.

Further confirmation of the collector performance was obtained when an alternative sampler was used, in which the collecting medium was chilled water. The collected spray was mixed with water flowing through a vertical double tube, open at the top end. The flow rate of water was about 20 times the sample collection rate. The solution formed was continuously withdrawn from the dryer. When collections were made less than 10 cm from the nozzle, this sampler yielded acetate retention values that differed from the standard collector measurements by less than 3% (absolute). At larger distances, the retentions obtained with the alternate collector fell below those measured with the standard collector, becoming 10% less at 15 cm (Kieckbusch, 1978). This was probably cased by surface losses resulting from deficient mixing with water and from the lower sample collection rate at greater distances.

SPRAY PATTERN

Swirl nozzles that produce a very fine spray, similar to the LN-1 nozzles employed here, are prone to exhibit anomalous spatial spray distributions. The nozzle internal design corresponds to a hollow-cone spray. However, as entrained air is drawn in by the spray, it easily drags the liquid drops of lower inertia from the outer regions of the spray inwards, causing the spray to contract (Rothe and Black, 1977). As a consequence, the spray produced by the LN-1 nozzle was usually of the solid cone type, with the maximum spray concentration at the center line. This behavior facilitated the collection but affected the drop size distribution (DSD), thereby complicating comparisons between different drying conditions.

The extent of the drag effects for each situation studied could be estimated from the measured flow rate through the collector, placed at the center line of the dryer. Different orifice inserts for the LN-1 nozzle gave center-line sample flows ranging from less than 2 to 20 g/min for 40% sucrose solution at a distance of 4 cm from the nozzle as the cone angle varied from 77 to 59 deg. Sample flows increased regularly with decreasing cone angle. Cone angles were measured photographically.

Differences in air and liquid density appeared to influence the entrainment effects considerably. Weaker drag power discriminated strongly in favor of entraining smaller particles. As an example, the DSD determined at the center line with an impaction droplet collector, 7 cm from the nozzle, indicated a Sauter mean diameter d_{vs} of 60.0 μm for a 20% sucrose solution, compared to 55.0 μm for a 40% sucrose solution (Kieckbusch, 1978). Experimental evidence (Lapple et al., 1967) indicates that d_{vs} of centrifugal pressure nozzles increases with increasing viscosity and therefore should be larger for the 40% sucrose solution. However, the drag effect is weaker for the 40% solution. Furthermore, these DSD determinations were performed with an ambient temperature air flow. Increasing the drying air temperature decreased the center line collected flow rate considerably. As a consequence of the weaker drag effect, an appreciable

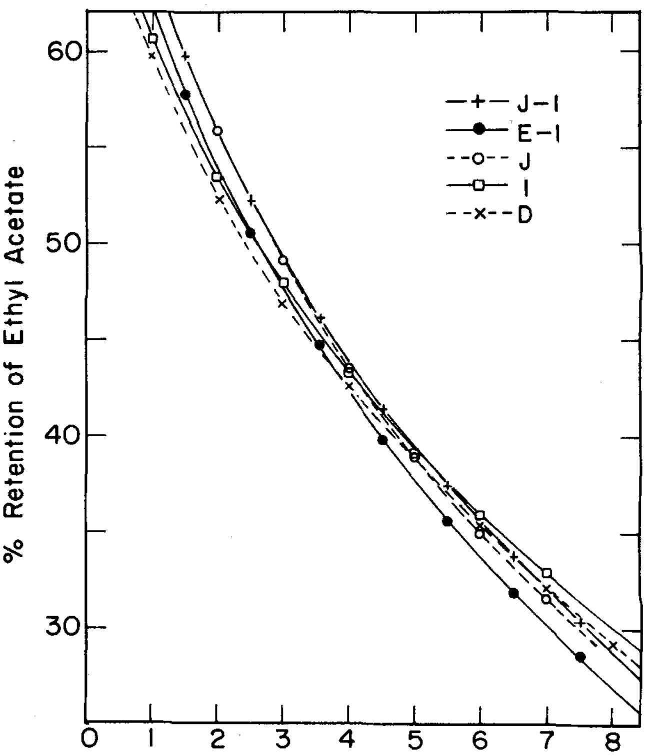

Figure 3. Retention of ethyl acetate for different orifice inserts (vs. evaporation). Forty percent sucrose solution, standard conditions. Cone angles: J-1, 59 deg; E-1, 60 deg; J, 63 deg; I, 64 deg; D, 62 deg.

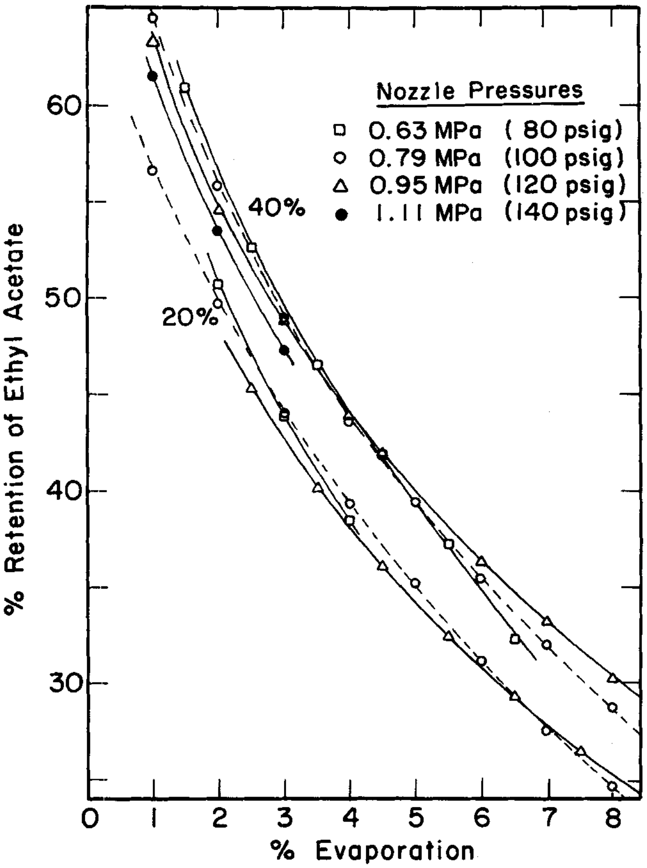

Figure 4. Retention of ethyl acetate at different nozzle pressures (vs. percent evaporation). Twenty and 40% sucrose solutions.

decrease in d_{vs} for both the 20 and 40% solutions would be expected under the actual operating conditions. The DSD under real drying conditions was not measured.

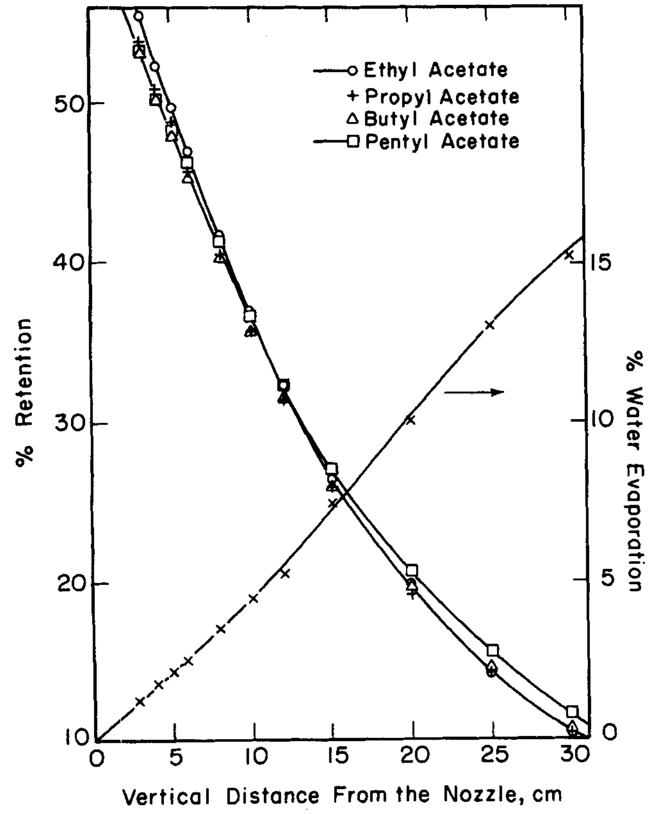

Figure 5. Retention of acetates and percent evaporation—1% sucrose solution, standard conditions; liquid flow rate = 6.4 L/h; insert 5.

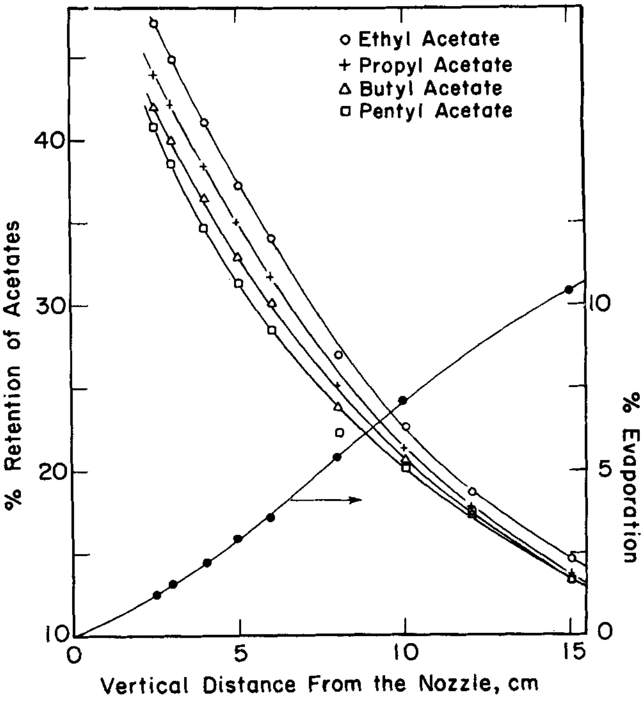

Figure 6. Retention of acetates and percent evaporation—20% sucrose solution, standard conditions; liquid flow rate = 6.75 L/h; insert J-1.

Effects of changes in DSD could be compensated for, partially, through the use of the experimental percent evaporation as a measure of selective effects of operating conditions on drop size. The percent evaporation can also account for differences in residence time due to variations in drop size and drop trajectory. It is recognized that variations in percent evaporation at a certain position cannot account fully for the effects of droplet entrainment and DSD on measured acetate retentions, since different degrees of gas and liquid phase mass transfer control are involved for water evaporation and loss of acetates. However, all

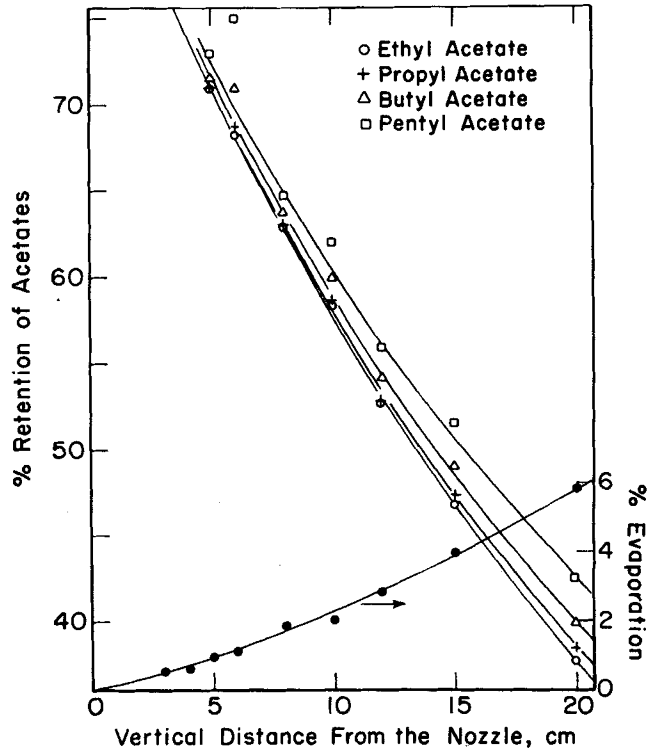

Figure 7. Retention of acetates and percent evaporation—40% sucrose solution, standard conditions; liquid flow rate = 6.95 L/h; insert J-1.

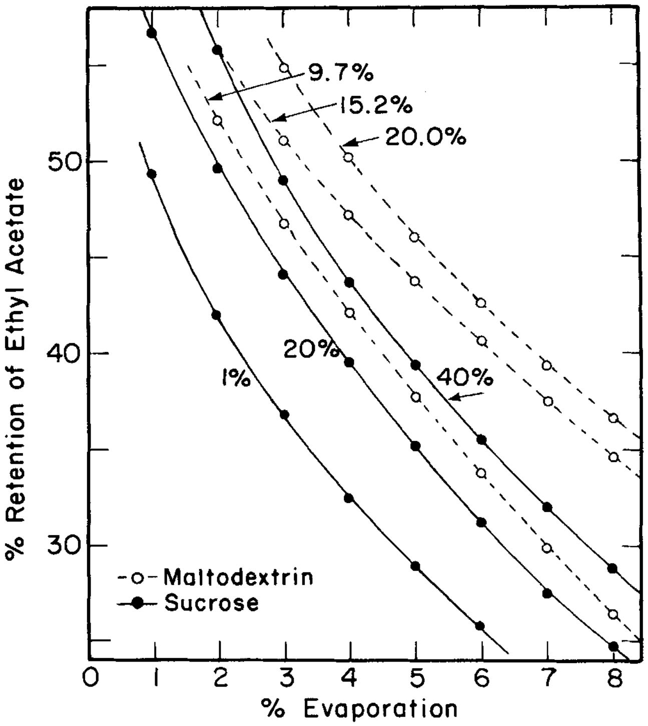

Figure 8. Retention of ethyl acetate during spraying of sucrose and maltodextrin solutions; standard conditions.

TABLE 2. BIOT NUMBER FOR ETHYL ACETATE TRANSFER IN SUCROSE SOLUTION AT 43°C

% sucrose	$H\left(\frac{\text{kPa}}{\text{kg-mole/m}^3}\right)$	Bi, drop	Bi, film
1	47	56	0.55
20	57	152	1.49
40	80	420	4.13

experimental results obtained in this investigation support the position that the percent evaporation can be used as a good first approximation to compare retentions of volatiles under different spraying conditions.

Measured lengths of the conical film before disintegration into droplets were of the order of 0.9 cm.

VOLATILES LOSS CHARACTERISTICS

The losses of acetates as a function of distance from the nozzle exhibit strong influences of operating conditions, nature of the feed solution and nozzle model. Even with the same model nozzle, changes in spray distribution produced by slight variations in nozzle cone angle affect the retention substantially. In the following discussion, each factor is considered separately.

Nozzle Design: Orifice Inserts

Figure 3 shows ethyl acetate retentions for different cone angles produced by different inserts with the LN-1 nozzle. A striking feature of the results shown in these and subsequent figures is the very large loss of volatiles at short distances from the nozzle, when the amount of water evaporated is still small.

These results support the use of percent evaporation as a first correction for differences in the diameters of collected spray particles and in residence time. The differences between results for different inserts are less than 5% (absolute) in Figure 3, whereas the spread in retentions at a given vertical difference is much greater. At 8 cm, retentions ranged from 33% for the D insert to 46% for the J-1 insert.

Nozzle Pressure

Experiments with 20 and 40% sucrose solutions, at 0.63, 0.79, 0.95 and 1.11 MPa (80, 100, 120 and 140 lb/in.^{2}gauge) atomizing pressure showed large differences in volatiles retention vs. distance, with larger gradients for retention vs. distance at higher nozzle pressure. Again, the differences are largely removed by plotting retention of ethyl acetate vs. percent water evaporated, as shown in Figure 4.

Concentration of Sucrose Solution

Figures 5 to 7 show the retentions of acetates and percent evaporation measured when 1, 20 and 40% sucrose solutions were sprayed with nozzle LN-1. The standard operating conditions were used.

A comparison of these figures reveals that there is a sharp increase in retention with increasing sucrose concentration; also, there is a selective gain in retention of higher molecular weight acetates over the lighter ones as the sucrose concentration increases. These are both direct results of the decrease in the diffusion coefficient of the acetates in the liquid with increasing sucrose content. The influence of the dissolved solids concentration is easily recognized in Figure 8, which shows the retention of ethyl acetate as a function of percent evaporation.

An examination of the relative retentions of the different acetates indicates an inversion in the order of retention. The 40% solution exhibits increasing retentions from ethyl to pentyl. The retention for the 1% solution increases from pentyl to ethyl, and the 20% solution has a mixed behavior. This pattern can be explained through the contributions of individual liquid and gas phase mass transfer coefficients to the overall mass transfer coefficient K_L as given by

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{Hk_G} \tag{1}$$

where k_L is the liquid phase mass transfer coefficient, k_G is the gas phase mass transfer coefficient and H is the Henry's Law constant. Both k_L and k_G decrease slightly with increasing acetate molecular weight, since the corresponding diffusion coefficients also decrease. H, however, increases strongly from ethyl acetate to pentyl acetate (Kieckbusch and King, 1979*b*; Kieckbusch, 1978). As a consequence, while k_L decreases only about 5% from acetate to acetate going up the homologous series, the corresponding increase of Hk_G is 20%.

The external gas phase resistance, however, should not play an important role in acetate transfer from drops. This can be deduced from the large values of the Biot number for drops, shown in the third column of Table 2. The Biot number (Bi) was calculated as $Bi = Hk_Gd/D_L$ or $Bi = H(Sh)D_G/D_{L\,RT}$, where H is the Henry's Law constant, R is the gas constant, T is absolute film temperature, D_G is gas phase diffusivity, D_L is liquid phase diffusivity, d is droplet diameter and Sh is the Sherwood number. The Sherwood number (k_GRTd/D_G) was taken to be equal to 2, corresponding to molecular diffusion from a spherical drop. An examination of the relative slopes of the retention curves in Figures 5 to 7 beyond 1 to 2 cm from the nozzle also leads to the conclusion that liquid phase diffusion controls acetate loss once drops are formed. The ratio of the slopes, between each acetate and that of next lower molecular weight is slightly higher than unity, about the same as the predicted ratio of k_L's.

The dominating control of the liquid phase for droplet mass transfer is not immediately recognizable from the relative positions of the curves for different acetates in Figures 5 to 7, since the cumulative loss is also affected by opposing conditions taking place very near the nozzle. The very small film thickness decreases the liquid phase resistance significantly. Estimates of the Biot number near the edge of the film are also given in Table 2 (fourth column). A film thickness of 5μm was assumed and was

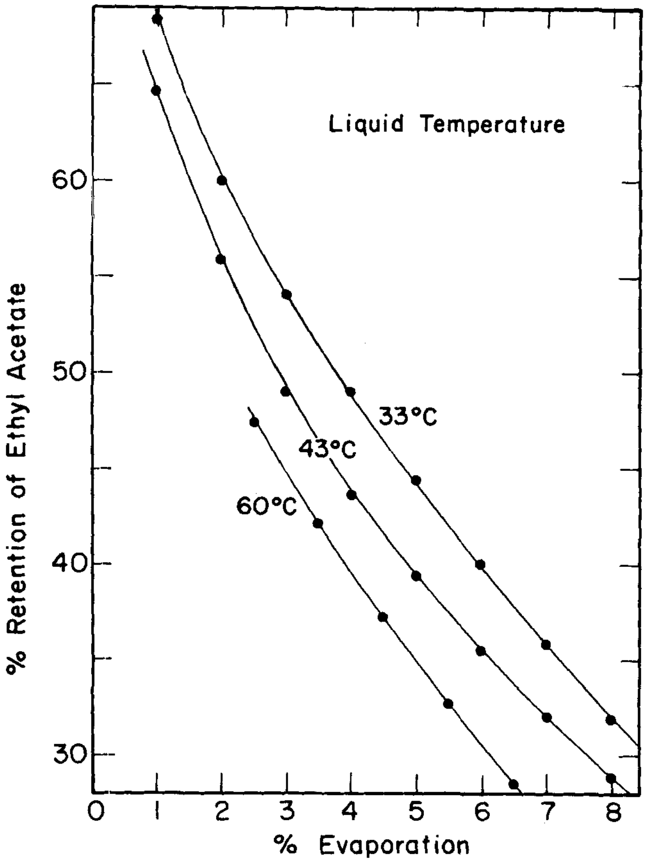

Figure 9. Retention of ethyl acetate at different liquid feed temperatures. Forty percent sucrose solution, T_{AIR} = 160°C, P= 0.79 MPa (100 lb/in.^{2}gauge).

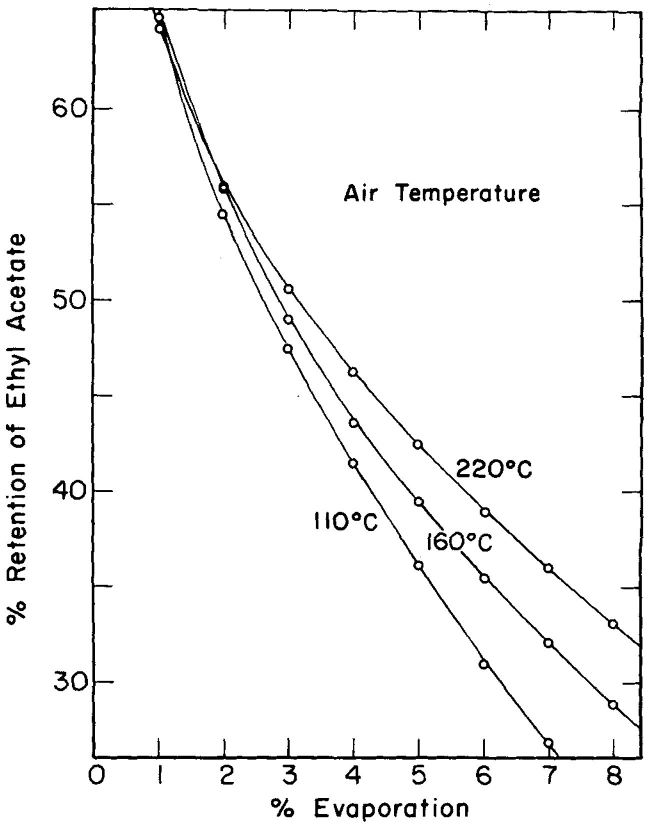

Figure 10. Retention of ethyl acetate, at different air temperatures. Forty percent sucrose solution, T_{LN} = 43°C, P = 0.79 MPa (100 lb/in.^{2}gauge).

used as the length dimension in the Biot number. The gas phase mass transfer coefficient was estimated using the boundary layer solution for mass transfer from a flat plate (Sherwood et al., 1977). The Bi values found indicate that the external resistance can provide an important fraction of the total resistance. In addition to losses from the film itself, the film disintegration should induce liquid turbulence and/or drop deformation and oscillation. These disturbances should reduce the liquid phase resistance to mass transfer to a greater extent than that in the gas. In view of the large effect of molecular weight on Hk_G, it is clear that even a moderate influence of gas phase resistance will suffice to invert the order of retention.

The influence of the gas phase resistance at short distances is clearly noticeable for the less viscous feeds (1 and 20% sucrose solutions), where retentions decrease from ethyl and pentyl. In the 40% solution, the retention at 4 cm from the nozzle already fits the liquid diffusion resistance order. The difference between the retention curves is small, however, suggesting an influence of gas phase resistance closer to the nozzle. After the drops are formed, liquid diffusion prevails, and the curves spread out.

For the 20% solution, the retention switches from the gas phase control order to the liquid diffusion control order. Pentyl acetate rises to become the highest retention during the early stages, but ethyl acetate settles down more slowly to become the lowest retention. As a result, the points at intermediate distances fall in an anomalous order of retention, with minimum retention occurring for propyl or butyl acetate. For 1% sucrose solution, larger losses during the drop formation period and higher liquid diffusion coefficients apparently delay the switch of the retention order to a distance greater than those monitored.

Maltodextrin

Mor-rex 1918 (CPC International) was used in concentrations up to 20%. Kinematic viscosity data indicated that a 10% maltodextrin solution had a viscosity similar to a 24% sucrose solution, and that a 20% maltodextrin solution was similar to a 42% sucrose solution (Kieckbusch, 1978).

The data for maltodextrin solution parallel those for sucrose solutions of corresponding viscosity, except that higher retentions are observed at a given percent evaporation (Figure 8). Part of this difference can be imparted to a reduction of H [of the order or 40% (Kieckbusch and King, 1979b)]. However, considerable reductions in liquid diffusion coefficients or substantial effects on drop size distribution are also required in order to explain the results.

Liquid Temperature at the Nozzle

Impingement measurements of the spray temperature using a small thermocouple indicated that the spray drops approach the wet bulb temperature within a few centimeters from the nozzle. Therefore, experiments with different liquid-feed temperatures should be another way of displaying the influence of the expanding film on the total losses.

Figure 9 gives ethyl acetate retention as a function of the water evaporation for the 40% sucrose solution for different liquid-feed temperatures. The increases in both the Henry's law constant and the liquid diffusion coefficient with increasing temperature increase both k_L and Hk_G in the film region and explain the large influence of the liquid-feed temperature on losses.

Air Temperature

A change in air temperature changes the wet bulb temperature of the spray. The film, however, would stay closer to the feed temperature. These factors should give only a small change in losses close to the nozzle, with larger changes further away as evaporation occurs under different thermal driving forces. Results for 40% sucrose solutions shown in Figure 10 confirm this reasoning. The spray temperature at a point 10 cm below the nozzle was measured with a small thermocouple and was found

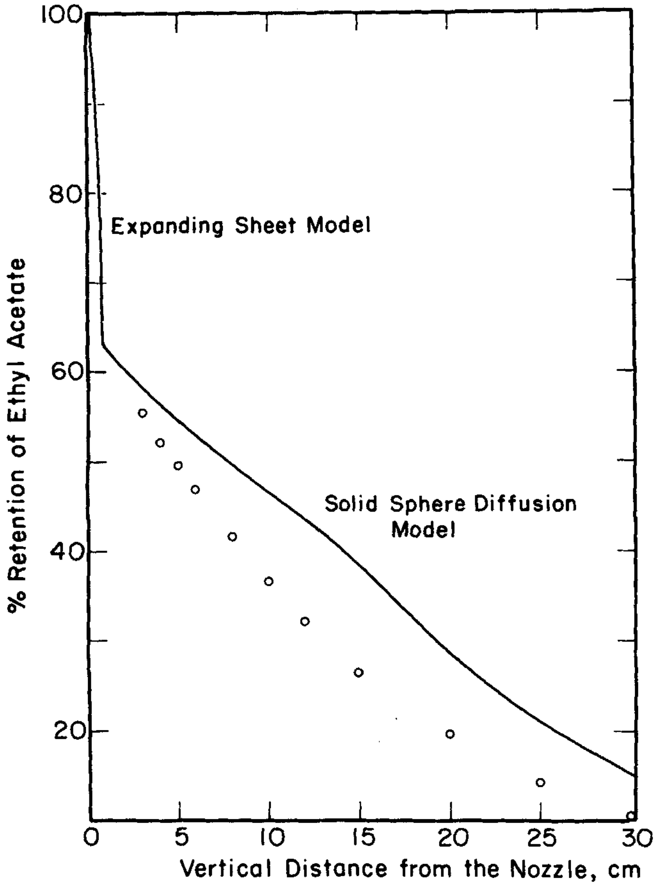

Figure 11. Comparisons of ethyl acetate losses with mass transfer models. Twenty percent sucrose solution.

to be 37° and 49°C for air temperatures at the nozzle level of 100° and 220°C, respectively. In the latter case, the air flow rate had to be reduced from 100 to 92 kg/h owing to limitations in air heating capacity.

These results lend strong support to the selective diffusion model. As evaporation proceeds, steeper water concentration gradients develop near the droplet surfaces at higher air temperatures, and the diffusion of acetates is thereby hindered. After equivalent losses in the film region, the curves therefore spread out, with higher retention at a higher air temperature. Results plotted vs. distance show much more spread near the nozzle.

Air Flow Rate

Experiments indicated no apparent effect on retention when the air flow rate was changed from 62 to 124 kh/h. The amount of water evaporated also remained virtually the same, as did the collected sample flow rate. The very large amount of air entrainment by the expanding spray appears to offset the hydrodynamic effects of a higher average air velocity.

Nozzle Design: Different Models

In addition to model LN-1, other pressure nozzles investigated included LN-1.5, LN-2 (hollow cone design), TG-0.3 (solid cone design) and T-400017 (fan nozzle). Results are given elsewhere (Kieckbusch, 1978). Retentions show a considerable variation from nozzle to nozzle at a given axial distance, but again show much less difference when correlated vs. percent water evaporation. Retentions for the different nozzles all fell within 3% (absolute) of one another.

Theoretical Models

Simpson (1975) and Simpson and Lynn (1977) used a laminar flow model to analyze liquid phase controlled mass transfer from the expanding film leaving a pressure swirl nozzle. Predictions of that model, for spraying 20% sucrose solution at standard conditions, are shown as the first, steeper curve in Figure 11. This curve ends at the point where disintegration of the film becomes most apparent, as measured photographically in the present work. From that point onward, a less steep curve gives the prediction of a model of diffusional loss from stagnant spheres, coupled with the particle dynamics model of Rothe and Block (1977), assuming the sphere diameter to be the Sauter mean value measured with ambient air, assuming the drops to be well mixed upon formation and assuming that the diffusion coefficient corresponding to the feed concentration is appropriate. Also shown in Figure 11 are experimental results for loss of ethyl acetate from 20% sucrose solution.

The combined model underpredicts the cumulative loss. However, the loss in the film zone appears to be predicted well, and the slope of the theoretical curve at greater distances agrees with that of the experimental curve rather well. The principal discrepancy appears to come in the vicinity of the film disintegration and the early droplet zones. This may reflect turbulence and drop deformation and oscillation. Very likely, the discrepancies also result from incorrect drop diameter and/or residence time, and/or from oversimplified averaging procedures. Furthermore, the model for the film zone neglects gas phase resistance, which should be important from Table 2. Substantial gas phase resistance in the film zone would reduce the predicted loss there; however, that effect could be compensated by turbulence in the film increasing k_L.

Reduction of Volatiles Loss

Preliminary attempts were made to use three different approaches for reducing the loss of volatiles in the vicinity of the nozzle. The first of these involved a conical shield for the film and early spray. It was found that the shield influenced the aerodynamics such that it was necessary either to leave a substantial gap between the shield and the spray or to operate with large droplets collecting and falling from the edge of the shield. The improvement in volatiles retention was small or negligible. Second, a gas stream saturated in propyl acetate was used to blanket the nozzle. The retention of propyl acetate was improved considerably by the resulting absorption, but not enough to warrant the extra consumption of propyl acetate in the blanketing gas. Finally, a vegetable oil emulsion was added to the liquid feed in an amount that would extract significant quantities of the acetates. This was found to reduce the loss of acetates considerably, as well as to alter the spray pattern by shortening the liquid film. This effect is receiving further study in continuing work.

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Multiplicity and Stability of the Hydrogen-Oxygen-Nitrogen Flame: The Influence of Chemical Pathways and Kinetics on Transitions Between Steady States

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Numerical bifurcation techniques are used to predict multiple steady states for a nonadiabatic, premixed hydrogen flame stabilized on a flat-flame burner. It is found that predicted conditions for burnout and ignition vary remarkably as rival chemical models are selected, while conditions for a well-stabilized flame are much less sensitive to chemical and kinetic assumptions. It is concluded that multiplicity theory can help define the chemical behavior of realistic, complex reaction-diffusion systems.

SCOPE

The use of theoretical predictions of multiplicity in the identification of kinetic parameters of combustion systems has been proposed by several workers (Smith et al., 1971; Fang et al., 1971; Williams, 1971; Berlad, 1973; Heinemann et al., 1979). Such an approach may be particularly useful for flames in which transitions between steady states correspond to the readily identifiable phenomena of burnout and ignition. We (Heinemann et al., 1979) have previously applied numerical bifurcation techniques (Keller, 1977) to a simple A → products flame and have shown that the solutions are particularly sensitive to changes in reaction rate coefficients near burnout.

In the present work, we apply such methods to the nonadiabatic, premixed, hydrogen flame stabilized on a flat-flame burner. Although the chemical mechanism of this flame is complex enough to afford a practical test of the use of multiplicity theory in discriminating between rival chemical pathways, the individual steps are well understood (Dixon-Lewis, 1970). Two mechanisms are studied: a seven-step mechanism involving hydroperoxyl radicals and a simple, four-step subset of the more complete model.

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