Continuous Drying of a Solid Wetted with Ternary Mixtures

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The influence on drying selectivity of the continuous-contact mode between a solid wetted with ternary mixtures and a gas stream was theoretically studied. The liquid mixtures, ethanol–isopropanol–water and water–ethanol–acetone, were used. A mathematical model describing a gas-phase-controlled process was developed, and the influence of the process variables was studied by simulations. In addition to the inlet composition of the moisture and temperature of the solid, gas composition has the most important effect on selectivity. Small changes of gas composition, either imposed or spontaneous, may modify completely the process trajectory. The extent of these effects depends on the ratio between the flow rates of inlet gas and liquid contained in the solid. Because of their effects on the evolution of temperature and composition, the operating pressure and energy sources other than convection are also useful in controlling the selectivity. Since all these variables determine the composition of the remaining liquid and thereby product quality, their influence should be predictable. The model may be a valuable tool for exploring the process, provided that drying is gas-phase-controlled.

Introduction

Drying products containing liquid mixtures convectively is often seen in the process industry. Some examples include drying of foodstuffs, pharmaceuticals, photographic films, magnetic storage media, varnish layers, coated laminates, and granulated synthetic material. The study of continuous drying operations is of interest because it is normally the method used by the industry unless the stuff to be dried is small in quantity or bulky in size. The particular feature of drying in a continuous convective process is the progressive change of the gas-phase composition and temperature along the contact path. If the solid contains a single solvent, the local drying rate decreases because of the diminution of the driving forces and transfer coefficients. When the solid contains solvent mixtures, the progressive enrichment of the gas during continuous drying may have effects on process selectivity, the other important variable that characterizes multicomponent drying. That is, the ability of the components to be removed from or be retained in the wet solid. The importance of selectivity stems from the influence of the residual composition on product quality. When, for example, foodstuffs are dehydrated, water must be removed and the volatiles that contribute to the aroma have to be retained. If a pharmaceutical product is dried, the aim is often to remove predominantly organic solvents, as the residual water content is normally demanded by subsequent processing of the product. The drying of coated films or laminates, and varnish layers, on the other hand, should be nonselective.

The selectivity during drying of a solid containing a liquid mixture is controlled by the interaction of gas-phase diffusion, phase equilibria, and transport within the solid. These processes are dependent on temperature and are thus influenced by the heat transfer. They are also affected by the contact mode between the phases. Schlünder (1982) analyzed the isothermal evaporation of a binary mixture to elucidate the conditions required by different controlling steps. Thurner and Schlünder (1986) extended the results to drying a porous

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solid containing the binary mixture isopropanol–water. A survey of this early work, including contact drying, was prepared by Schlünder (1988). The effect of a third component of negligible volatility, and gas preloading was studied by Riede and Schlünder (1990a,b), gas-phase-controlled drying of solids wetted with ternary and multicomponent mixtures was analyzed by Martínez and Setterwall (1991); liquid-side control for a binary mixture was reported by Pakowski (1990); the multicomponent case was studied by Martínez (1990); and recent developments in the area have been reported by Pakowski (1994). All these investigations concern processes where the gas conditions do not change during the process. This is often the case in batch drying when the gas greatly exceeds the evaporated moisture. Continuous drying of solids containing liquid mixtures is scarcely treated in literature. Keey (1978) has analyzed multistage dryers for a solid containing a single solvent, allowing for different flow types. Drying continuous-sheet materials with a film-coating of single organic solvents has been studied by Chen and Wang (1981); they emphasize contactless sealing methods and include the simulation of a multistage unit. Thurner and Wischniewski (1986) studied the drying of polyvinyl alcohol wetted with a binary mixture in a closed-circuit dryer using experimental drying curves and sorption isotherms to determine the belt area of the dryer and the final moisture content. They assumed constant drying conditions. Martínez (1990) has simulated a multistage dryer for solids containing multicomponent liquid mixtures with parallel and impingement flow. That work was focused on the effect of the flow type on the overall drying rate, not on the selectivity. In the present work, we consider the influence on selectivity of the progressive changes of the gas-phase composition and temperature along the contact path in a continuous gas-phase-controlled drying process. This condition is normally achieved by drying materials at low drying rates. An analysis with simulations revealed that the combined effects of inlet gas composition, inlet liquid composition, the inlet ratio between gas and liquid mass flow rates, conduction heat, and total pressure may be useful in controlling drying selectivity.

Theory

The rate of evaporation or condensation due to the continuous contact between a hot gaseous stream and a wet solid moving in parallel can be studied by looking at the simultaneous mass and heat transfer between the bulk of the phases and a gas–solid interphase of variable composition and temperature. The mass and heat transfer between the phases depend on the transport in the gas phase, the conditions at the interphase, and the mechanism of mass and heat transfer within the solid. Depending on the mass- and heat-transfer rates, the process may be controlled by the gas side, thermodynamic equilibrium, or the solid side.

Mass and energy balances

The resistance of the solid phase may be neglected at sufficiently low transfer rates. In this case, the nonexistence of temperature and concentration gradients in the solid in the direction perpendicular to the interphase and the assumption that the bulk gas is well mixed except at a thin layer immediately beside the interphase, imply that the changes of temperature and composition of both phases along the contact path will be a direct result of the net flow of energy and mass that is interchanged between the two phases and the surroundings, as shown in Figure 1.

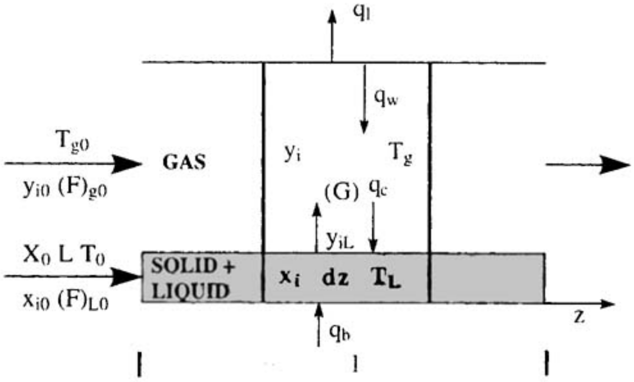

Figure 1. Volume element for mass and heat transfer.

Mass Balances. Under these conditions the solid does not exert any influence on mass transfer and may be disregarded in the mass balances. A mass balance over the small volume element leads to the following expressions for the liquid and gas phases:

$$\frac{d(F)_L}{dz} = -a(G) \tag{1}$$

$$\frac{d(F)_g}{dz} = a(G), \tag{2}$$

where (F) is the vector of the number of moles passing through the contact device per unit time and cross section; (G) is the vector of molar evaporation fluxes; a is the contact surface per unit volume; and the subscripts L and g denote the liquid and the gas phases. If the gaseous mixture consists of n components and one of them is a noncondensable gas of low solubility in the liquid, there are $n-1$ equations expressing the change in the number of moles with the distance in each phase, one for every condensing component.

Energy Balances. Because of its heat capacity the solid cannot be regarded as inert from the energy point of view, and the solid flow will appear explicitly in the energy balance for the wetted solid. The energy balance over the same volume element yields for both phases:

$$\frac{dT_L}{dz} = \frac{a\left\{q_c + q_b - \sum_{i=1}^{n-1} G_i\{H_{ig} - H_{iL}\}\right\}}{\sum_{i=1}^{n-1} F_{iL}c_{iL} + LC_s} \tag{3}$$

$$\frac{dT_g}{dz} = \frac{a\{q_w - q_l - q_c\}}{\sum_{i=1}^{n} F_{ig}c_{ig}}, \tag{4}$$

where T is the temperature; c_i is the molar heat capacity of the component i at constant pressure; H is the molar enthalpy; q is the heat flux; the subscripts c and b in the heat fluxes denote the flux transferred by convection between the phases and the heat that reaches the wetted solid by conduction or radiation from the walls of the contact device; and q_l and q_w represent heat losses and a possible contribution to the energy of the gas phase from the walls. Except for the presence of the solid, this model is similar to a model for a well-mixed liquid that was experimentally verified by Vidaurre (1992).

Mass- and heat-transfer rates

Mass Transfer. Mass transfer in multicomponent systems exhibits particular interactions between the diffusing species. When a ternary mixture evaporates into an inert gas, the mass transfer in the gas phase involves a quaternary mixture. If diffusional interactions are considered, the following expression may be used to calculate the molar fluxes:

$$(G) = [\beta][k][\Xi]\{(y)_L - (y)\}, \tag{5}$$

where matrix $[\beta]$ incorporates the convective contribution into the mass transfer; $[k]$ is the matrix of zero-flux mass-transfer coefficients; and matrix $[\Xi]$ is the matrix of the correction factors, which accounts for the influence of finite mass-transfer rates on the diffusion fluxes. The driving force is the vector of composition differences between the interphase and the bulk of the gas. For details about the calculation of the fluxes, see Taylor (1982).

Heat Transfer. Convection is considered the main mechanism of heat transfer. The heat flux may be written

$$q_c = \alpha \Xi_h (T_L - T_g), \tag{6}$$

where α is the heat-transfer coefficient at zero mass flux, and Ξ_h is the correction factor that accounts for the effect of finite mass fluxes on the heat-transfer coefficient. For the method of calculation, see Bird et al. (1960). A similar expression describes the other mechanisms of heat transfer, provided proper transfer coefficients are used. Conduction, radiation, and losses by free convection do not involve any correction factor.

Mass- and Heat-Transfer Coefficients. For a flat geometry and streamlined flow, the results of boundary-layer theory are used to calculate mass- and heat-transfer coefficients at zero mass-transfer rate. Depending on the length of the contact path, the transition to turbulent flow may occur. The Chilton-Colburn analogy is applied in this case. For details see Coulson et al. (1991).

Coupling between the phases

The coupling between the phases that permits calculation of the gas composition at the interphase as a function of the liquid composition in the solid is achieved by assuming that phase equilibrium is reached instantaneously at every point of the interphase. Since the solid is not hygroscopic, only vapor–liquid equilibrium is of interest

$$y_{iL} = \frac{x_i \gamma_i p_i^0}{p_T}, \tag{7}$$

where γ is the activity coefficient; p^0 is the saturation pressure of the pure component; and p_T is the total pressure.

Boundary conditions

Equations 1 to 4 represent a set of $2n$ ordinary nonlinear differential equations that permit the calculation of the composition and temperature of the wet solid and the gas phase at any position along the contact path. This is an initial-value problem where the location is related to the residence time in the dryer by the solid linear velocity and inlet conditions correspond to initial values. If the liquid and gas have a uniform composition at $z = 0$, the following conditions are applicable:

$$(F)_L = (F)_{L0} \quad \text{at } z = 0 \tag{8}$$

$$(F)_g = (F)_{g0} \quad \text{at } z = 0 \tag{9}$$

$$T_L = T_{L0} \quad \text{at } z = 0 \tag{10}$$

$$T_g = T_{g0} \quad \text{at } z = 0. \tag{11}$$

Drying selectivity

The changes in moisture composition during contact with the gas phase will be determined by the selectivity of the process. The selectivity, S_i, is defined as the difference between the relative molar evaporation flux of component i, and the molar fraction of component i in the liquid x_i:

$$S_i = \frac{G_i}{G_T} - x_i. \tag{12}$$

Depending on the value of selectivity, the following can be stated:

- $S_i > 0$, component i is removed preferentially, and its molar fraction in the moisture decreases.
- $S_i = 0$, the evaporation of component i is nonselective, and its molar fraction in the moisture remains unchanged.
- $S_i < 0$, component i is not removed preferentially, and its molar fraction in the moisture increases.

It may be inferred from Eq. 12 that the selectivity will depend on the instantaneous or local values of liquid composition, liquid temperature, gas composition, and the air velocity.

A particular feature of gas-phase-controlled evaporation into a noncondensing gas is that a nonselective process may occur at liquid compositions that are different from a thermodynamic azeotrope. This is possible because, in the presence of a noncondensing gas, the process is not only dependent on phase equilibria but also on diffusion in the gas phase. Martínez and Setterwall (1991) found the relationships between the relative volatilities and the effective mass-transfer coefficients that make the process nonselective for a mixture of $n-1$ condensing components:

$$\nu_{ij} \frac{k_{i,\text{eff}}}{k_{j,\text{eff}}} = 1 \quad i = 1, \ldots, n-1 \quad j = i+1, \ldots, n-1, \tag{13}$$

where ν_{ij} is the relative volatility, and $k_{i,\text{eff}}$ is the effective mass-transfer coefficient. When diffusional interactions are considered, the liquid composition which, under certain kinetic conditions, produces nonselective evaporation, can be obtained from the following general expressions:

$$\{S_i + x_i\} \sum_{j=1}^{n-1} \sum_{k=1}^{n-1} f_{jk}\{\gamma_k p_k^0 x_k - p_T y_k\}$$

$$- \sum_{k=1}^{n-1} f_{ik}\{\gamma_k p_k^0 x_k - p_T y_k\} = 0 \qquad i = 1, \ldots, n-1, \quad (14)$$

where f_{jk} are the elements of the correction matrix for multicomponent mass transfer. To determine the dynamic azeotropes during evaporation into a pure gas, Eqs. 14 must be solved with selectivities equal to zero and a gas free of solvents. If these conditions have to be maintained during an entire process, the evaporation must also be isothermal. As suggested by Eqs. 14, gas composition has a great influence on selectivity, which means it can be used to control its magnitude. For instance, the selective evaporation process of a liquid mixture in contact with a pure inert gas may be modified to a nonselective evaporation by preloading the inert gas with an appropriate composition of volatiles. Also, any finite selectivity may, in principle, be obtained by choosing adequate loading conditions calculated according to Eqs. 14. In another approach, Pakowski (1992) searched for dynamic azeotropes and determined their stability by plotting the entropy production rate of the evaporating liquid. The method is applicable to a gas of constant conditions.

The main difference in a continuous process is that the gas composition in Eqs. 14 varies spontaneously with the contact path and depends on the evaporation process itself. Consequently, only the inlet process conditions can be controlled by preloading the gas.

Results and Discussion

Two liquid systems were used as moisture in the calculations: ethanol–isopropanol–water and water–ethanol–acetone. The first system comprises species with selectivities of similar magnitude, whereas the selectivity of acetone, in the second system, is much greater compared to the other components. To gain some insight about the expected behavior of the liquid systems in a continuous process, the local values of selectivity were calculated and the influence of some variables was examined.

Zero-selectivity of the liquid systems

The calculations of the selectivities of the liquid mixtures are based in Eqs. 12 and 14. In order to accelerate the convergence of the evaporation fluxes, a first estimate of the corrected fluxes calculated according to an explicit expression developed by Burghard and Krupiczka (1975) was introduced. The activity coefficients were computed by means of the Wilson equation, with constants given by Gmehling and Onken (1982). Other physical properties of pure components and mixtures were estimated using standard methods described by Reid et al. (1987). The zero-selectivity curves for the liquid systems evaporating into pure nitrogen at two different temperatures are shown in Figure 2.

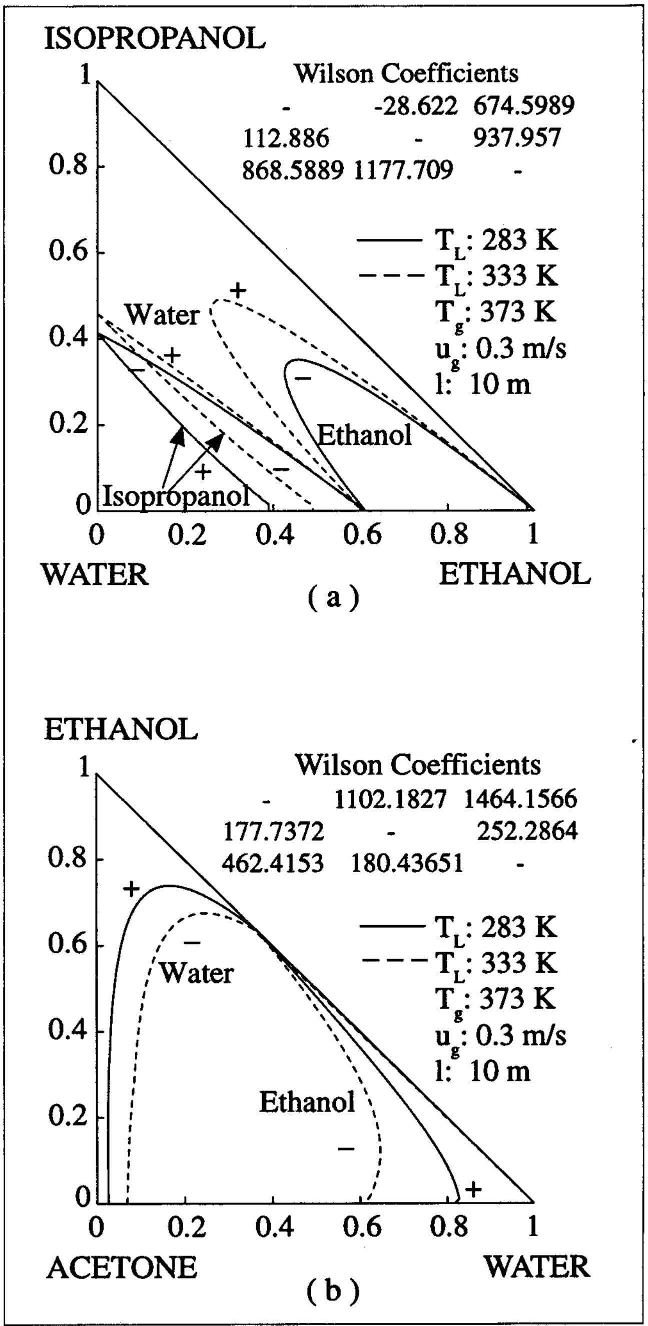

Figure 2. Zero-selectivity curves as a function of liquid composition and temperature; isothermal evaporation into pure nitrogen.

The zero-selectivity curves define the boundaries between the zones of positive and negative selectivity for each component of the mixture and are valid at a given set of process conditions. The different zones of selectivity reveal that liquid composition greatly influences selectivity. It used to be negative in the zones adjacent to the corner of pure components. It is remarkable that in the ethanol–isopropanol–water system, the selectivity of water is positive in a large domain of liquid compositions in spite of its comparatively low volatility. This factor is evidently offset by the high diffusion coefficient of water vapor. This system exhibits two dynamic binary

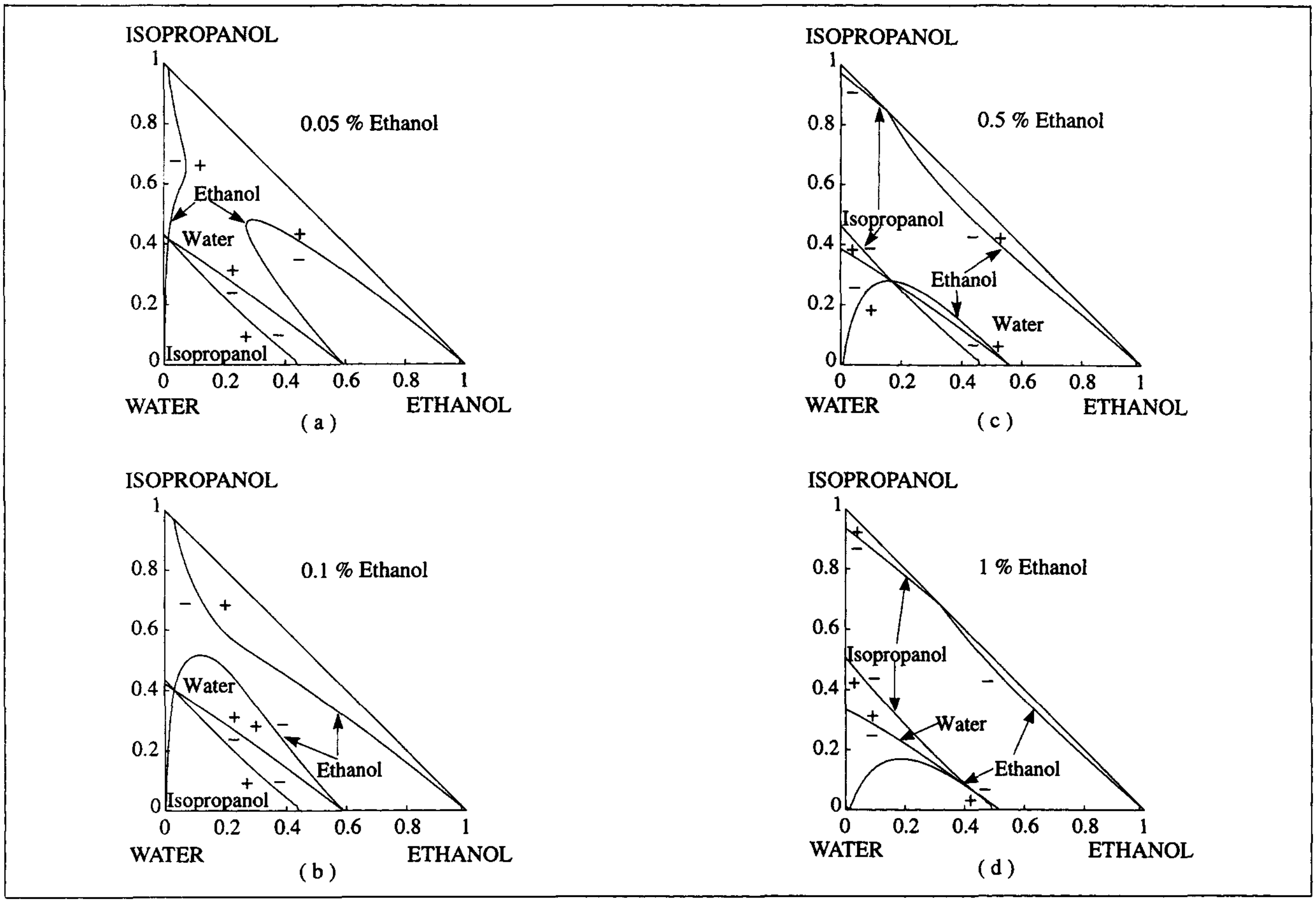

Figure 3. Influence of the gaseous concentration of ethanol on selectivity.

azeotropes: isopropanol–water and ethanol–water at the liquid composition where the respective zero-selectivity curves intercept. The system does not present any ternary dynamic azeotrope. The volatility of acetone in the other system is so high that its selectivity is positive over the whole range of liquid compositions. The liquid-phase temperature also has a significant influence on the process selectivity. This influence is expressed in the displacement of the boundaries between the zones of positive and negative selectivity. An increase in temperature seems to reduce the selectivity of the most volatile. In the first system, the negative zone of ethanol expands with temperature while in the second, the negative zones of ethanol and water are reduced, and the selectivity of acetone is less positive. This is not visible in Figure 2 because the selectivity of acetone is always positive.

The great influence of gas composition on selectivity may be observed in Figures 3a to 3d, which represent zero-selectivity curves of a liquid mixture evaporating into a gas loaded with ethanol.

The sequences of increasing gas preloading with ethanol show that the vapors in the gas cause large displacements of the zero-selectivity boundaries and the appearance of new zones. An interesting result is the appearance of ternary dynamic azeotropes when the air contains ethanol. In fact, an infinite number of ternary dynamic azeotropes is encountered as the concentration of ethanol in the gas increases. The liquid composition of the ternary dynamic azeotrope is then shifted from the binary dynamic azeotrope isopropanol–water to the binary dynamic azeotrope ethanol–water. Even the position of the binary dynamic azeotropes is affected by the composition of the gas. The presence of the other solvents in the gas has similar effects, vapors of a certain species having the major influence on its own selectivity, which tends to be reduced, but also on the selectivity of the others. These effects are less pronounced, however, and may act in any direction. This behavior can be inferred from the derivative of selectivity with respect to gas composition:

$$\frac{\partial S_i}{\partial y_k} = \frac{1}{G_T}\left\{\frac{G_i}{G_T}\sum_{j=1}^{n-1} f_{jk} - f_{ik}\right\}. \qquad (15)$$

Unless the system is strongly interactive, the main coefficients are considerably greater than the cross coefficients. The main coefficients are always positive, whereas the cross coefficient may be positive or negative. The sign of the derivative will be determined by the main coefficients. If the selectivity derivative is with respect to the molar fraction of the same component in the gas, the negative second term will determine the sign of the derivative. In the other cases, the sign will be determined by the first term, which depending on the cross coefficients and liquid composition, may lead to a positive or negative derivative.

The great influence of gas composition makes the preloading of the gas a convenient method to control selectivity when the changes of gas conditions are negligible. In continuous processes, where the inlet conditions are normally not preserved for the whole length of the contact path, the possibility of controlling the evolution of the process by preloading the gas is limited by the spontaneous changes occurring during the operation.

The gas velocity and gas temperature have less influence on selectivity, and its local value may be considered independent of these factors. They have, however, a decisive influence on which phase controls the transfer processes, since high gas velocities normally imply high transfer rates in the gas phase, and this may induce the appearance of resistances in the liquid phase.

Simulations

We examined the influence of the process variables on the selectivity of a continuous process using the simulations performed at different process conditions. Owing to the nonlinearity of the dynamical system described by Eqs. 1 to 4, they were solved numerically. A fifth-order Runge-Kutta method with adaptive step-size control of local truncation error was used. All calculations were performed assuming cocurrent flow between the phases and that nitrogen was the inert gas. The variables examined were inlet-gas composition, inlet-liquid composition, inlet ratio between gas and liquid mass flow rates, conduction heat, and total pressure. Cocurrent flow was chosen to obtain a gentle drying regime. The choice is not only related to the conditions of a gas-phase-controlled process. Although the overall separation is favored by countercurrent flow, cocurrent contact is the most convenient method to dry thermolabile substances, since in this regime the warmest gas first makes contact with the cold and wet material.

Influence of the Inlet-Gas Composition. The effect of the spontaneous changes occurring in the continuous process was compared with a process where the gas conditions remain constant. Since these conditions are often satisfied in batch drying, that case was called the batch case. The trajectories in Figure 4 show that a batch process starting at a liquid composition yielding selective evaporation of water was reserved to obtain preferential evaporation of ethanol and isopropanol by preloading the inlet gas with ethanol. Simulation of the continuous process reveals that in this case, selectivity is also reversed in comparison with the unloaded case, but even though the final stage is almost the same as that of the batch case, the process trajectories are different. Since separation processes normally do not run to completion, the final product will usually contain a mixture. The differences in the remaining composition achieved by different trajectories may thus have a decisive influence on product quality. The ratio between the inlet-gas and -liquid flow rates, $R_0 = F_{g0}/F_{L0}$, determines if a continuous process approaches a batch. To increase the ratio is equivalent to reducing the impact that mass and heat transfer between the phases have on the gas conditions. A continuous process approaches a batch process when this ratio goes to infinity.

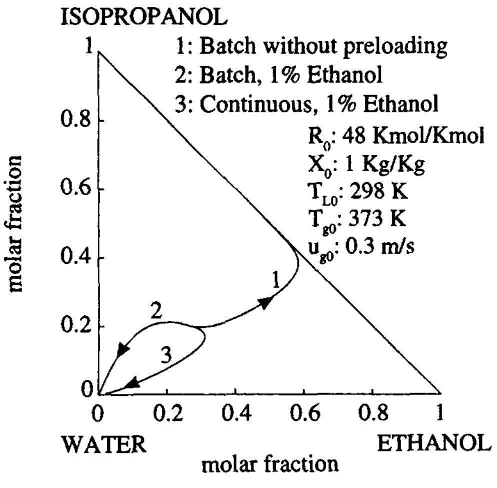

Figure 4. Effect of the contact mode on gas preloading.

Influence of the Inlet Moisture Composition. Since the zone from which the process starts is defined by the inlet liquid composition, this variable must certainly greatly influence the process evolution. However, as discussed earlier, the role of the spontaneous changes that characterize a continuous process may also be influenced by varying the inlet ratio between the gas and liquid flow rates.

Results of simulations starting from different locations in the domain of liquid compositions and the ratio R_0 as parameter are shown in Figure 5.

Note that the zero-selectivity curves plotted together with the process trajectories correspond to the inlet conditions. All the simulations were performed for the ethanol–isopropanol–water system with an inlet gas free from vapors. As the R_0 ratio goes to infinity, the process trajectories seem to approach the limit compositions of either pure water or pure isopropanol. Which of these limits is reached depends on the selectivity zone from which the process started. These final stages are denoted as stable dynamic azeotropes (Pakowski, 1992), in the literature on multicomponent drying, because they constitute poles of attraction for all trajectories. The ethanol–isopropanol–water system seems to have only two such poles. The corner of pure ethanol concentration never seems to be reached, irrespective of which zone the process is started from. In fact, the corners of pure-component concentrations are nodes of the dynamical system described by Eqs. 1 and 3 with constant transfer coefficients. This represents the batch case. The nodes are determined from the critical points or stagnation points of the differential equations, and their stability can be estimated by analyzing the residue curve map of the dynamical system. This approach was used by Foucher et al. (1991) to study a simpler case of azeotropic distillation. In the continuous case, however, the composition diagrams are only part of the phase space of the system since a complete description requires seven dimensions. Furthermore, since the transfer coefficients are dependent on z, the differential equations are not autonomous and the critical points are dependent on the position along the dryer. Consequently, as R_0 diminishes, the trajectories are modified and they do not reach any of the stable nodes of the batch system. At the lowest ratios, the changes in gas composition along the contact path are considerable and equilibrium between the phases may be reached, the evaporation being stopped and the remaining liquid composition being at the

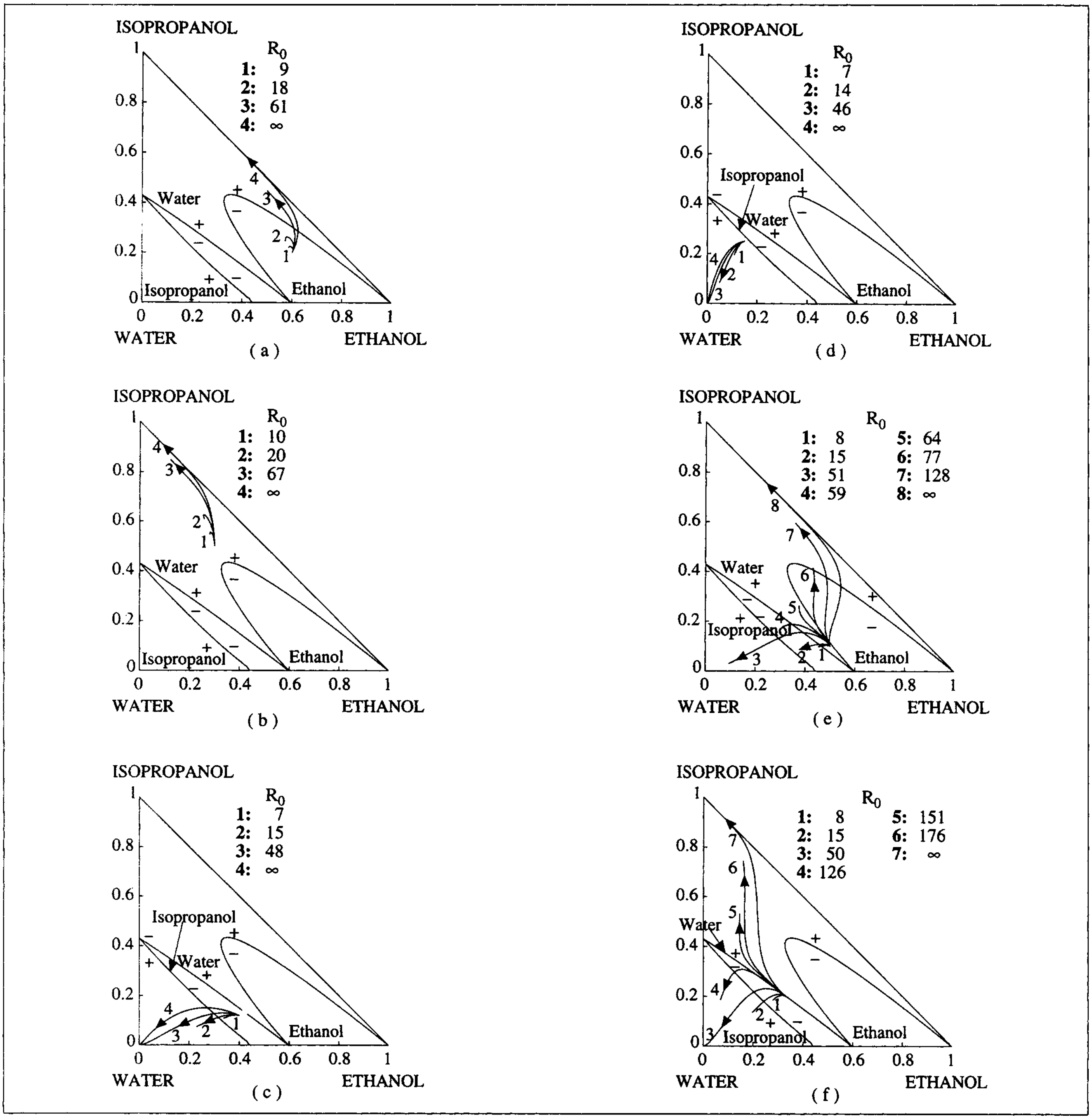

Figure 5. Influence of inlet moisture composition and the gas–liquid flow-rate ratio on process trajectories.

equilibrium composition. At intermediate ratios, the liquid may evaporate completely, but the last liquid mixture evaporates at a different composition than that of the pure components. Although in most cases the process follows a trajectory that agrees with what could be expected from the selectivity diagram corresponding to the inlet conditions, there are zones where the R_0 ratio may have more unexpected effects. This can be observed in Figures 5e and 5f, where processes starting at some of the boundaries in the selectivity diagram were simulated. A relatively moderate change in the ratio R_0 forced the process into a trajectory toward the opposite stable node of the batch process. This phenomenon may be better understood if we examine the zero-selectivity curves at some of the intermediate stages of the trajectories where the departure occurs.

In the trajectory described in Figures 6a to 6c, the process evolves toward a zone of negative selectivity for water at an early stage. A negative selectivity for water forces the process to the corner of pure water. This effect is reinforced by the positive selectivity of ethanol. The initially negative selectivity of isopropanol is not able to reverse this evolution. Furthermore, the selectivity of isopropanol becomes gradually less negative and finally acquires a positive value. At this stage the process inevitably follows a trajectory toward the corner

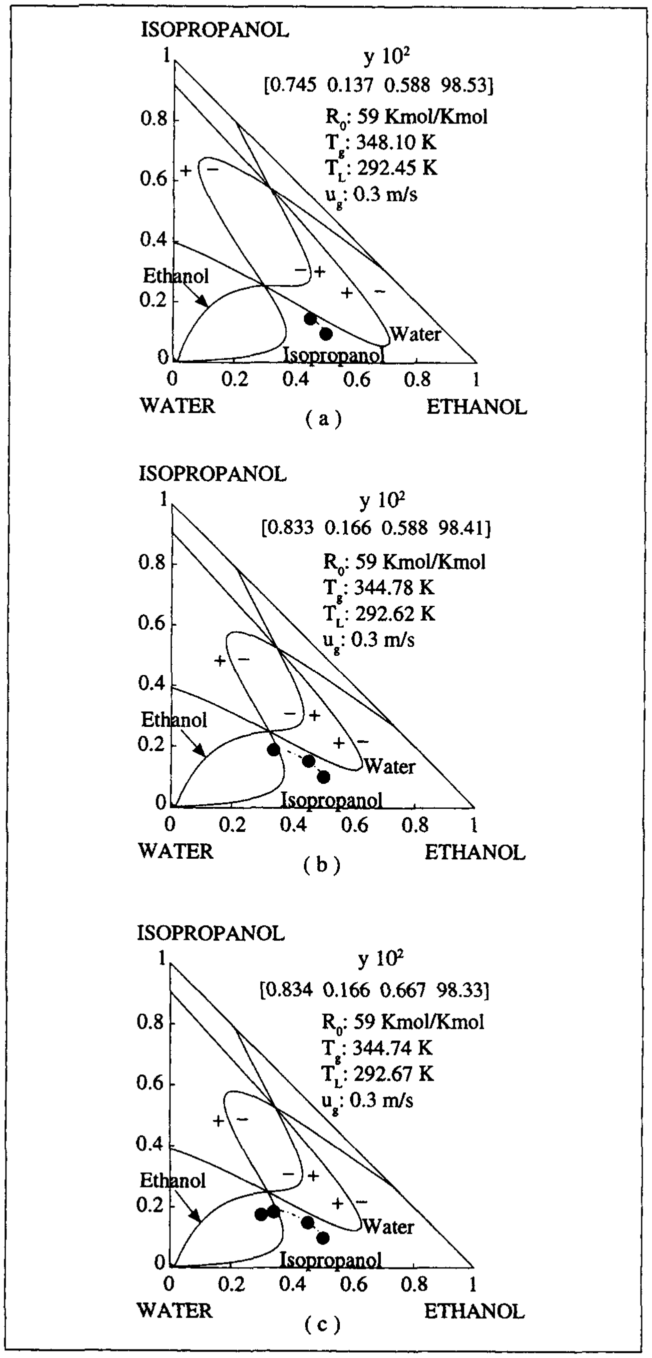

Figure 6. Zero-selectivity curves at intermediate stages of trajectory 4 in Figure 5.

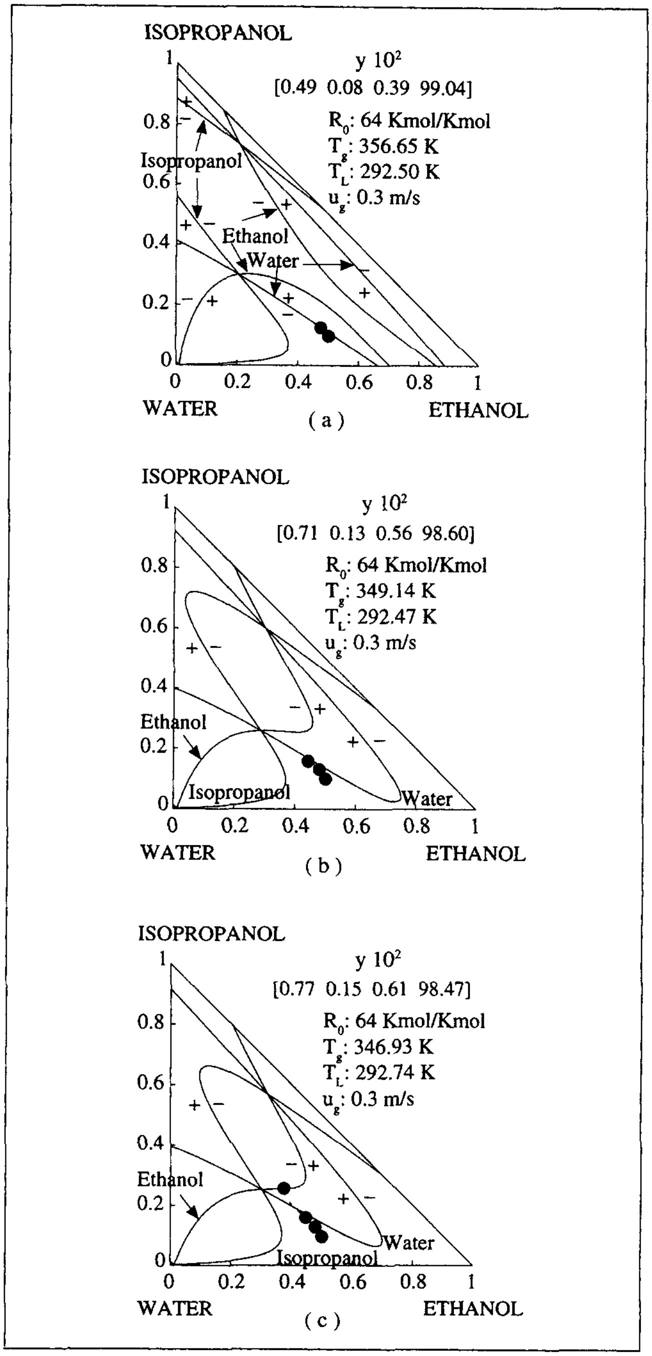

Figure 7. Zero-selectivity curves at intermediate stages of trajectory 5 in Figure 5.

of pure water. In the process described in Figures 7a to 7c, on the other hand, the selectivity of water always remains close to the zero-selectivity boundary. When it is at the negative side it is only slightly negative. The stronger effect of the negative selectivity of isopropanol now forces the process toward the corner of pure isopropanol. The weak positive selectivity of ethanol reinforces this tendency. Finally, when the process reaches a zone of negative selectivity for ethanol, it is not able to influence the trajectory because isopropanol selectivity is much more negative and the process definitely evolves toward the corner of pure isopropanol.

When examining the evolution of selectivity in the spontaneous process, it is impossible to separate the effects of the changes of liquid temperature and gas composition. As discussed before, the liquid-phase temperature also influences process selectivity. However, its effect is less pronounced than that of the gas composition, particularly at the level of spontaneous changes in liquid temperature that may be expected in continuous processes. These changes of temperature in a continuous process depend on the balance of the energy fluxes and the selectivity itself. The process may, to some extent, be influenced by the inlet temperatures. If they are such that the convective heat is less than is necessary to sustain the evaporation, the temperature of the solid will drop. In the opposite case, the temperature of the solid will rise. These changes, which may occur in a relatively short part of the contact path, depending on the heat capacity of the phases and how far the inlet temperatures are from the equilibrium temperatures, will be slowed as a state of balanced energy flux is approached. A constant temperature, however, will never be reached unless the composition at this stage corresponds to a dynamic azeotrope. Further changes in the temperature of the solid will be determined by changes in liquid composition. If the remaining liquid is enriched with a component with a high boiling point, the liquid temperature will increase. If the selectivity is such that components with low boiling points are not removed first, the temperature will decrease. Although the changes in liquid temperature are gradual, they may also cause significant displacement of the selectivity zones.

Effect of the Conduction Heat. An additional energy flux by conduction may alter the balance of convective energy fluxes and thereby the evaporation temperature. The liquid system water–ethanol–acetone is involved in the manufacture of some thermolabile pharmaceuticals. In this case, a low concentration of acetone and ethanol is desirable in the final product. These products are frequently dried at low pressure, sometimes using a weak air stream to eliminate the moisture. In these conditions it is likely that an important contribution to the heat reaching the wet solid comes from the body of the dryer by conduction. The simulations shown in Figure 8 show that an additional conductive contribution may significantly influence the final composition of the moisture.

The comparison is based on a final liquid content of 0.02 kg/kg. The different additional energy contributions were achieved by using increasing heat-transfer coefficients by contact with a hot surface of constant temperature. Since the heat fluxes are not constant during the process, average values are shown. As a corresponding mechanism for mass transfer does not exist, the heat flow by conduction results in a higher solid temperature during the drying process, as displayed in Figure 8b. A solid with a higher temperature increases the selectivity of water and is, in principle, unfavorable for the evaporation of the most volatile components. Even though the effects are not as pronounced as the variables examined before, they may be enough for the final product to exceed the limits of an admissible concentration of organic solvents. The results also depend on the final liquid content and the R_0 ratio, as shown in Figure 8c. The molar fraction of acetone in the remaining liquid is higher at a higher temperature in a wide range of liquid content, while at low values of liquid content the removal of acetone is favored by the conductive contribution to heat transfer. Although, it does not seem possible to infer the correct values of these variables *a priori* to get the expected final liquid composition, they may be used to control selectivity.

Influence of the Total Pressure. Like gas velocity and gas temperature, the total pressure hasn't much influence on the local selectivity. It has, however, decisive influence on drying temperature, and thus on process evolution (see Figure 9b). The behavior of the local selectivity shown in Figure 3 suggests that a lower pressure should favor the early evaporation of the component with the lowest boiling point. The simulations displayed in Figure 9a confirm that the removal of acetone is significantly improved by lowering the pressure. The comparison is based on a final liquid content of 0.05 kg/kg. In this case, results corresponding to Figure 8c show that the same tendency toward lower acetone concentration would be obtained irrespective of the final liquid content. Since the main effects are due to liquid temperature, the changes in gas composition are less important and the ratio R_0 has less influence.

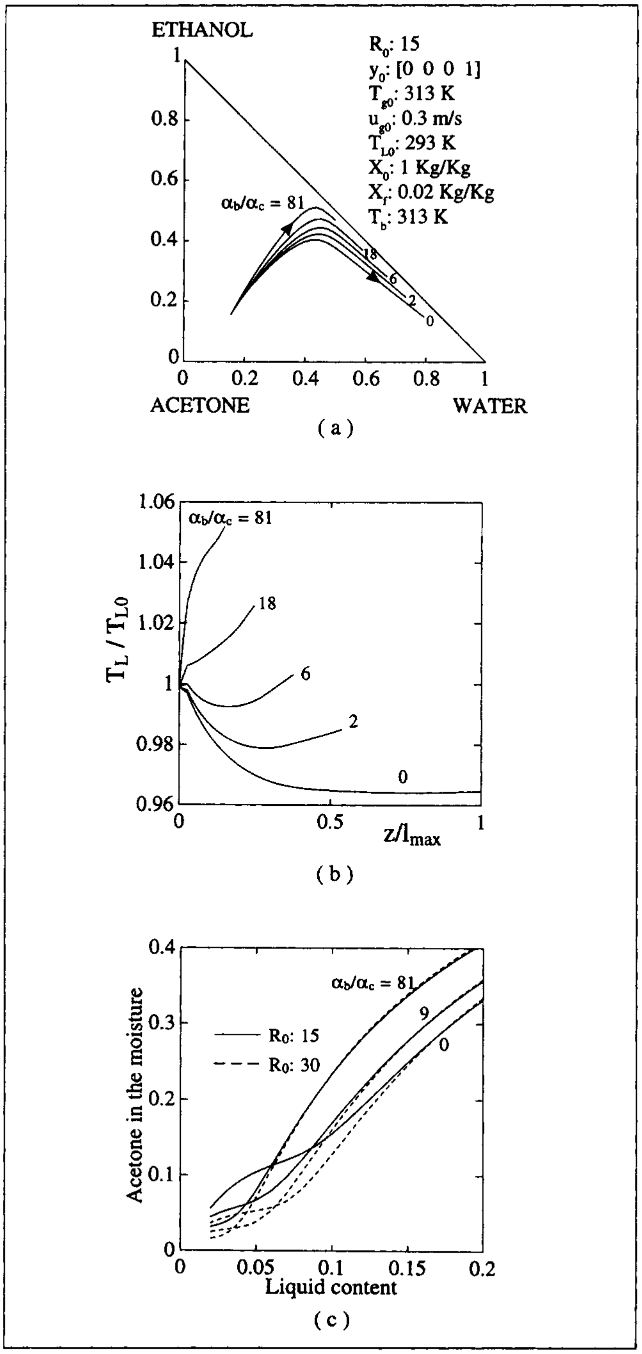

Figure 8. Influence of conduction heat on the process trajectories.

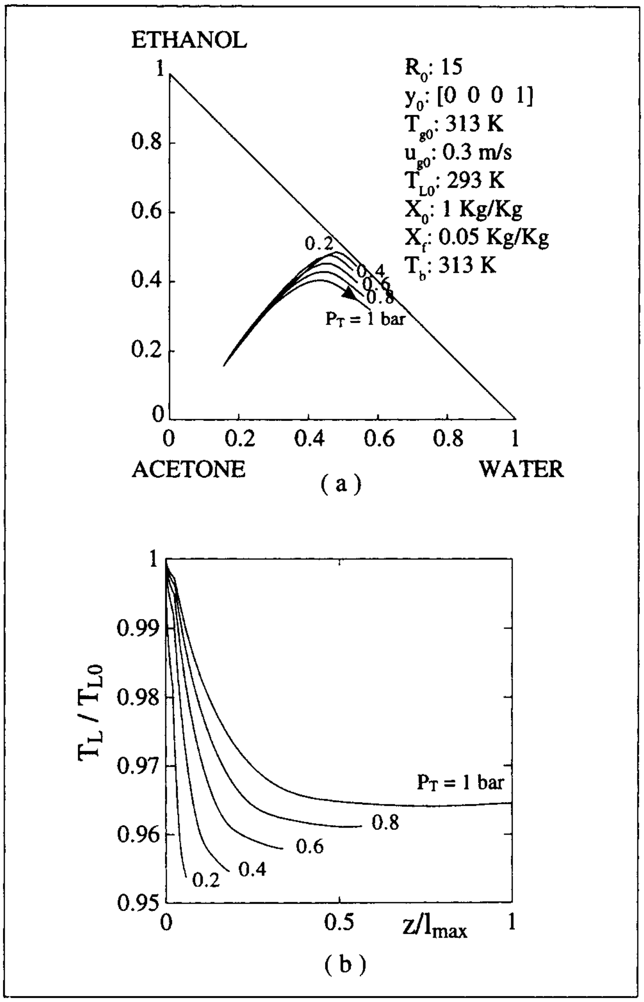

Figure 9. Influence of the total pressure on the process trajectories.

Controlling Step. The extent to which the conditions used in the simulations correspond to a gas-phase-controlled process can be estimated by utilizing the criteria developed by Schlünder (1982), and later extended to a more general case by Riede and Schlünder (1991). The distinction between gas-phase-controlled evaporation and a process governed by phase equilibrium involves the gas-side number of transfer units defined according to

$$\mathrm{NTU}_{g,i} = \frac{a\{k_{i,\mathrm{eff}}\}_g}{F_g}. \tag{16}$$

where NTU is the number of transfer units. At low gas flow rates, F_g, the $\mathrm{NTU}_{g,i}$ goes to infinity and the process is completely controlled by equilibrium. Under these conditions, no modifications of the equipment or kinetics can achieve residual liquid compositions precluded by equilibrium. In the reverse case, when the gas flow rates are high, the $\mathrm{NTU}_{g,i}$ tends toward zero. In that case, mass transfer on the gas side can be the controlling step, provided the so-called liquid-side kinetic separation factor becomes unity. This factor is defined as

$$K_{L,i} = \exp\left\{ -\frac{G_T}{\{k_{i,\mathrm{eff}}\}_L} \right\}, \tag{17}$$

and is close to unity when the resistances to mass transfer in the liquid phase are negligible. This is likely to occur at low total evaporation rates. When the liquid side controls the process, $K_{L,i}$ goes to zero. The original analysis concerns a binary and isothermal liquid mixture and, since, in a binary mixture, the diffusion coefficients are identical, only a single liquid-side kinetic separation factor appears. In the general case, there will be as many such factors as there are independent diffusing species in the mixture. If, however, only the order of magnitude is of interest, using an approximate mass-transfer coefficient in the liquid phase is enough for the analysis. The drying rates and separation factors shown in Figures 10a and 10b correspond to the highest drying rates obtained with the acetone–ethanol–water system and a simulation performed with high gas velocity. The order of magnitude of the mass-transfer coefficient in the liquid phase was

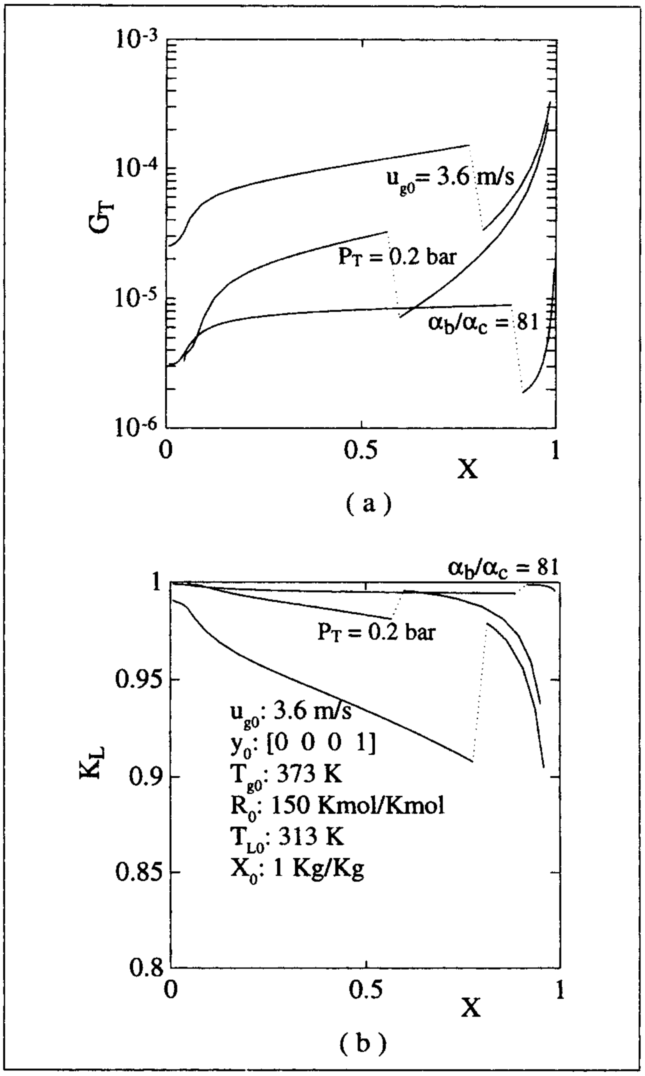

Figure 10. Extent of the liquid-side control of the process.

estimated to be about 10^{-3} kmol/m^2·s. The discontinuity corresponds to the transition to turbulent flow.

It is clear that even at a high gas velocity, liquid phase resistance is low. The difficulties of achieving conditions of a liquid-side-controlled process seem to be related to the mode of contact. In parallel flow, the transfer coefficients and driving forces decrease rapidly along the dryer, and a very high gas velocity must be used to obtain high evaporation rates. This is not necessarily valid for other forms of contact. In impinging drying, for instance, the process will rapidly be controlled by the liquid side, since it involves many more higher external transfer coefficients. Note that the analysis concerns a gas in contact with the liquid phase and may be considered approximately valid for a saturated solid. In considering a solid, the transfer coefficients within the solid should be used in Eq. 17, and they diminish rapidly when the solid becomes less saturated. Consequently, Eq. 17 should produce solid-side control at lower drying rates than does evaporation from a liquid-free surface. The conditions of a gas-phase-controlled process would be satisfied when drying under a gentle drying regime of thin solids and when the moisture is superficially distributed. In general, different mechanisms will dominate the process during different stages of continuous drying, and frequently the effects will be combined. Since the final composition of the mixture will depend on the whole process, knowledge of the asymptotic behavior derived for batch drying is of very limited use in predicting the final composition of the mixture.

Conclusions

The ratio between the inlet gas and liquid flow rates, R_0, is of crucial importance for the evolution of selectivity during the continuous, convective drying of a multicomponent moisture. As this ratio increases toward infinity, the continuous process approaches that of a batch process. The conditions of the gas phase are then considered constant, and all the properties of the behavior of selectivity in a batch process may be applied.

The ternary liquid mixtures ethanol–isopropanol–water and acetone–ethanol–water exhibit two stable dynamic azeotropes each when evaporating into a gas with constant conditions: pure isopropanol or pure water in the first case, and pure ethanol or pure water in the second case. They can only be reached in a continuous process if the inlet ratio between the gas and liquid flow rates goes to infinity. The liquid systems do not exhibit ternary dynamic azeotropes when evaporating into a pure gas.

The presence of vapors in the gas, achieved either spontaneously or by preloading, has a great influence on the local selectivity. Ample displacement of the zero-selectivity curves, appearance of new zones, and the presence of multiple ternary dynamic azeotropes may be obtained.

A continuous process may to some extent be controlled by preloading the inlet gas. The effect is, however, limited by the influence of the spontaneous changes in the gas conditions. You have a better chance of controlling the process by preloading the inlet gas when the ratio, R_0, is high.

The temperature of the solid also influences process selectivity. This influence appears in the displacement of the boundaries between the zones of positive and negative selectivity, but not in the appearance of new zones. Although spontaneous changes in the temperature of the solid are gradual in continuous processes, the displacement of the selectivity zone may be decisive for the evolution of the process.

Although the operating pressure and other sources of heat transfer have a limited influence on the local selectivity, they significantly influence the way the temperature changes during the process. In general low pressures favor selectivity of the most volatile components, whereas heat transfer by conduction has the opposite effect.

Since small changes in R_0 may lead to completely different process trajectories, the final stage may not, in general, be determined *a priori* in a continuous process. At low ratios, the saturation of the gas may be reached and the evaporation cease when the composition of the remaining liquid reaches equilibrium. At intermediate ratios, the liquid may evaporate completely.

Since the last composition of the mixture normally has a decisive influence on product quality, the trajectories should be predictable. The present model may be a valuable tool for simulating the continuous drying of solids wetted with multicomponent mixtures as long as the process is gas-phase-controlled.

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Notation

C = heat capacity per unit mass, kJ·kg^{-1}·K^{-1}
K = separation factor
L = solid flow rate, kg·s^{-1}·m^{-2}
l = characteristic length, m
u = linear velocity, m·s^{-1}
X = liquid content, kg liquid kg solid^{-1}
y = molar fraction in the gas phase, kmol·kmol^{-1}
z = length coordinate, m
[ ] = square matrix
( ) = column vector

Subscript

h = heat transfer

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