Pore-network study of the characteristic periods in the drying of porous materials

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Abstract

We study the periods that develop in the drying of capillary porous media, particularly the constant rate (CRP) and the falling rate (FRP) periods. Drying is simulated with a 3-D pore-network model that accounts for the effect of capillarity and buoyancy at the liquid–gas interface and for diffusion through the porous material and through a boundary layer over the external surface of the material. We focus on the stabilizing or destabilizing effects of gravity on the shape of the drying curve and the relative extent of the various drying periods. The extents of CRP and FRP are directly associated with various transition points of the percolation theory, such as the breakthrough point and the main liquid cluster disconnection point. Our study demonstrates that when an external diffusive layer is present, the constant rate period is longer.

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1. Introduction

The drying of porous media is a process of significant scientific and industrial interest. Applications abound in areas such as pharmaceuticals and foodstuff, the wood and paper industries, ceramics, polymers and other materials. It is also associated with the recovery of volatile oils from the subsurface and soil remediation. The drying problem involves several mechanisms that apply at the pore scale and affect the macroscopic behavior of the drying process. Among others, these include phase change at the liquid–gas interface, mass and heat transfer by diffusion and convection, capillarity-induced flow through wetting films and the receding of the liquid–gas interfaces under the combined viscous, capillary and buoyancy forces.

Due to its importance, a plethora of studies have addressed various aspects of drying. Originally, the problem was approached from a phenomenological point of view. Under this approach, the porous medium is replaced by a hypothetical effective continuum, in which the detailed physics at the pore scale are lumped into averaged quantities. Equivalent-continuum partial differential equations are used to describe the temporal and spatial evolution of volume-averaged quantities. Equivalent-continuum partial differential equations are used to describe the temporal and spatial evolution of volume-averaged quantities, such as moisture content. Closure to the problem is provided using mostly empirical parameters (for example, see [1] for a detailed presentation).

A significant improvement in modeling has been achieved in recent years through pore-network studies. These have contributed to our understanding of how phenomena occurring at the pore level influence processes at the larger scale. Starting with the pioneering work of Fatt [2] pore-network models have been used to study two-phase or multi-phase displacement in porous media. In the last ten years, these have been extended to phase-change processes in porous media including boiling (e.g., [3]) and solution-gas drive (e.g., [4,5]). Drying
is a special case of phase-change and has been studied at the pore-network level by Nowicki et al. [6], Prat [7,8], Laurindo and Prat [9,10], Prat and Bouleux [11], Huinink et al. [12], and Yiotis et al. [13–16]. These models have offered insight in the physics involved and now provide a valuable tool for understanding macroscopic properties.

In this paper we use a 3-D pore-network model to study the effects of gravity and of an external diffusive layer on the shape of the drying curve. We identify four distinct drying periods and associate these periods with various critical percolation points: the breakthrough (BT) and the main cluster disconnection (MCD) points (see [17] for a review of percolation theory). The main goal of this work is to offer better insight in drying processes by interpreting the macroscopic drying regimes in the context of percolation theory.

2. Background

The drying of porous materials can be macroscopically characterized by the drying curve, which is a plot of the recovery rate of the volatile species as a function of the liquid saturation within the porous medium. Typically, at the early stages of the process the rate remains almost constant. This period, known as the constant rate period (CRP), is characterized by an excess of liquid at the surface pores of the porous material [18–20]. During the CRP, capillarity controls the liquid flow from inside the pore space to the product surface, where the liquid evaporates. The liquid flows through either completely or partially wet pores, where either the pore walls are covered with liquid films or fluid remains at the corners and the central part of the pore is dry.

The CRP is followed by the falling rate period (FRP), during which the recovery rate decreases rapidly. During the FRP, drying is controlled by mass transfer through the dry pore space. At the beginning of the FRP, mass transfer through the dry part of the porous medium takes place under isothermal conditions, as the pore walls remain sufficiently wet and the local temperature is in equilibrium with the vapor concentration. This is known as the first FRP. As the liquid films evaporate, an “unfavorable” temperature gradient develops from the product surface to the bulk of the porous material (the temperature being higher closer to the product surface where the liquid saturation is lower). This produces an excessive mass transfer resistance toward the product surface and the drying rates decrease more rapidly, as the product surface becomes dry [21]. This is known as the second FRP.

In typical industrial applications, the porous material is subject to the flow of a purge gas along the external porous surface, which can significantly enhance the recovery process and reduce drying times. The volatile components evaporate at the liquid–gas interfaces inside the pore space and are transferred to the external surface by diffusion and convection. As the liquid–gas interface recedes deeper in the porous medium, its movement is controlled by capillary, viscous and buoyancy forces. Depending on the process conditions, each of these forces may be dominant over the others [13]. For example, in slow drying processes and when gravity is negligible, capillarity is controlling. In this case the movement of the interface can be accurately described with invasion percolation, assuming that the spatial distribution of pore sizes is random [7,8]. In this approach, the liquid–gas interface is theoretically a fractal (rather than flat or slightly rough) object. When gravity is not negligible, which is the case for very dense liquids in large 3-D pore networks, however, capillarity controls the interface only over a finite length scale. Over larger length scales, buoyancy forces become dominant and control the interface properties. In such a case, its movement is described with the invasion percolation in a gradient model [22–24].

Two important transition points in drying are related to the position of the liquid–gas interface: the breakthrough (BT) and the main cluster disconnection (MCD) points. The breakthrough point occurs when the gas phase first reaches the side opposite to the open side (percolates) and a sample-spanning gas cluster forms for the first time. From this point on, sample-spanning clusters for both the gas and the liquid exist simultaneously in the porous medium. During this period of drying, most liquid pores belong to the sample-spanning liquid cluster (main liquid cluster, MLC) and only a very small percentage of liquid pores belong to isolated liquid clusters (disconnected clusters, DC). The second point, the main cluster disconnection point, occurs when the largest liquid cluster in contact with the product surface loses contact for the first time and becomes “finite.” At this point the MLC breaks up in smaller disconnected clusters (DCs) and the average size of these clusters becomes smaller in time as the liquid evaporates at every cluster interface.

The main objective of the paper is to describe the physics of the drying process during the CRP and the first FRP in the context of percolation theory and associate the transition points in the invasion percolation model with the characteristic drying regimes with emphasis on the effect of gravity and of the external mass transfer, assumed here to be diffusive.

3. Description of the model

3.1. Preliminaries

While several authors have studied drying using 2-D pore-network models (e.g., see the Introduction for references), the literature on 3-D pore-network studies is very limited. The work of Le Bray and Prat [25], based on a 3-D invasion percolation without trapping model (IPnoT), is the only one that also includes phase change at the gas–liquid interfaces and diffusive transport of the evaporating species. These authors reported results from only one realization on a $51 \times 51 \times 51$ pore network (due to the computationally intensive nature of the 3-D simulations). Le Bray and Prat [25] argue that 3-D simulations are required to study the various regimes that develop during drying and that the CRP that appears in their simulation is a distinctive feature of 3-D drying, where trapping is not important, contrary to 2-D simulations, where the role of trapping is significant and a CRP does not exist.

The simulation in [25] shows that the drying curve is characterized by 4 periods (reproduced in Fig. 1): A first period,
Fig. 1. Schematic reproduction of the Le Bray and Prat [25] drying curve. Four drying periods are distinguished: An initial drying period (1), a constant rate period (CRP) (2), a falling rate period (FRP) (3), and a receding front period (RFP) (4). Associated with a rapid drop in the drying rate that ends just before the gas breakthrough (BT). This is followed by the constant rate (CRP) and the falling rate (FRP) periods. The fourth period begins after the liquid cluster loses contact with the open side of the pore network (main cluster disconnection, MCD) and is characterized by the receding of the drying front. Le Bray and Prat [25] associate the transition between the CRP and the FRP with a transition in the rate of cluster formation. They argue that small liquid clusters at the product surface empty at faster rates than clusters deeper in the porous medium, leading to a decrease in the surface saturation at higher rates closer to the surface. However, Le Bray and Prat [25] do not comment on the critical surface saturation that marks the transition from the CRP to the FRP. They also argue that the CRP is longer in larger pore networks, because the number of pores occupied by gas and neighbor liquid pores per number of sites at the interface should scale as $L^{0.5}$, where $L$ is the lattice size. Their results offer a qualitative insight in the drying of porous media under constant external conditions.

Other authors simulate drying processes in porous media using invasion percolation with trapping models [26,27]. These models do not solve for the concentration field in the gas phase and, therefore, do not produce drying curves. The computational cost in such approaches is significantly reduced, allowing for simulations on larger 3-D pore networks. However, the results apply only to the structural properties of the liquid clusters.

Several authors [21,28] have shown that the local mass transfer coefficient at the product surface also depends on the mass transfer conditions above the external surface of the porous material. In general, these conditions depend on the surface moisture of the medium, among other parameters. Therefore, for a realistic solution of the drying problem, the external mass transfer problem must be solved in conjunction with the mass transfer within the pore network. In the present work, we account for the effect of the external drying conditions by considering only diffusion over the product surface through a layer with a finite size. At the top of this diffusive layer the vapor pressure of the liquid component vapors is taken equal to zero.

3.2. Implementation

We consider the isothermal drying of a 3-D cubic pore network that is initially saturated with a volatile single-component liquid. The top side of the pore network is open to the ambient environment, while all other sides are impermeable to mass transfer. The pore network consists of pores connected through throats. The size of each pore and throat is characterized by its radius, which is selected at random from a uniform size distribution at the beginning of the process. The pore/throat sizes are not correlated. We assume that the average volume of the pores is significantly larger than the volume of the throats.

A diffusive layer of thickness $d = N \times l$, where $l$ is the distance between two neighboring pore centers in the pore network and $N$ is an integer, lies over the product surface. The mass transfer coefficient $h_s$ at the open side of the pore network is defined by the local liquid vapor flux through the diffusive layer,

$$Q = h_s(C_s - C_\infty),$$

where $Q$ is the flux, and $C_s, C_\infty$ are the vapor concentration at the surface of the pore network ($x = 0$, see Fig. 2 for a schematic) and the ambient environment, respectively.

At any time during the process, the liquid component in the pore space at the liquid–gas interface evaporates and is transferred by diffusion through the porous medium and the diffusive
layer toward the ambient environment. Steady-state diffusion is assumed to describe this transport,

\[
D \nabla \cdot (A \nabla C) = 0,
\]

where \(D\) is the local diffusion coefficient and \(A = \pi r^2\) is the throat cross section. The following boundary conditions are assumed,

\[
C = C_e \quad \text{at the interface liquid pores}
\]

and

\[
C = 0 \quad \text{at the pores located at the top of the diffusive layer},
\]

where \(C_e\) is the equilibrium concentration of the liquid vapors.

As the liquid phase volume decreases, the liquid–gas interface inside the porous medium recedes following invasion percolation without trapping. When gravity is negligible, the interface adjacent to the throat with the larger radius is invaded. The gas phase grows in a fashion very similar to drainage (Fig. 2).

In the presence of gravity the invasion rule must be modified to account for buoyancy. The capillary pressure \(P_c\) along an interface throat is equal to

\[
P_c = P_g - P_L = \frac{2\gamma}{r} + \Delta \rho g_v h,
\]

where \(g_v\) is the component of gravity acceleration in the direction of displacement, \(r\) is the throat radius, \(h\) is the distance from a reference level for gravity, \(\gamma\) is the interfacial tension, and \(\Delta \rho\) is the difference in density between the two fluids. The relative intensity of gravity over capillary forces is typically expressed by the Bond number \(B\),

\[
B = \frac{\Delta P_{\text{grav}}}{\Delta P_{\text{cap}}} = \frac{\Delta \rho g_v l r}{2\gamma},
\]

where \(l\) is the characteristic pore length.

During the process, continuous liquid clusters become disconnected from the initial liquid cluster and surrounded by the gas phase. Evaporation takes place at the interface of these clusters as well, and the liquid pores are invaded following the same rules that apply for the main liquid cluster (MLC). The number of pores that are being emptied simultaneously at each time step is equal to the number of liquid clusters including the MLC.

4. Numerical results

We used the pore-network model to simulate drying under various conditions. Specific emphasis was placed on two effects, so far not explored in previous studies: the effect of gravity and the effect of mass transfer outside the porous medium. The effect of gravity is stabilizing when the receding phase is heavier and the gravity acts in the same direction. It is destabilizing otherwise. We note that effects of films, which can be significant [15], were not accounted, but will be considered in a future work. Film flows, particularly in the presence of gravity, add a degree of complexity that requires a separate analysis. First, we consider the base case in which there is no gravity or an outside diffusive layer.

\[\text{(Fig. 2).} \]

Fig. 3. Three-dimensional phase distribution patterns at 80, 60, 40, and 20% liquid saturation. Liquid clusters are shown in gray color. Liquid vapors escape from the top side of the network. \(B = 0, d = 0\).

4.1. Drying in the absence of gravity \((B = 0)\) and in the absence of an external diffusive layer \((d = 0)\)

We performed a series of numerical simulations using 80 \(\times\) 80 \(\times\) 80 pore networks in the absence of gravity and of a diffusive layer. The network is assumed initially occupied by liquid hexane. The simulations terminated when 90% of the liquid was recovered from the network. Each simulation required approximately 18 h on an Intel Xeon 3.6 GHz workstation. Simulations on larger networks require significantly more time (e.g., 100 \(\times\) 100 \(\times\) 100 pore networks required several days per run).

Fig. 3 shows the evolution of the phase distribution patterns at four different time steps corresponding to 80, 60, 40, and 20% overall liquid saturation. The structure of the liquid clusters is characteristic of invasion percolation. In particular, Fig. 3d is characteristic of the receding front period (RFP) identified by Le Bray and Prat [25]. During the RFP a dry region develops close to the open side and a two-phase region away from it. The liquid saturation in the latter appears to be almost constant with respect to distance. Evaporation occurs from the liquid clusters at the interface between the dry and the two-phase region, while liquid clusters deeply in the two-phase region make a negligible contribution to the drying rates because the nearby gas phase remains almost saturated.

Fig. 4 shows a characteristic drying curve. At the beginning of drying, the rate decreases sharply due to the evaporation from pores located at the outlet end. The average front position increases rapidly and almost linearly with the liquid saturation. This period can be associated to an excess of liquid at the product surface. According to percolation theory, the associated saturation decrease would be negligible for large systems.
In addition, in most typical drying processes this period would last over a negligibly small interval, due to the presence of a diffusive layer over the product surface (see Section 4.2).

When the BT is reached, the liquid–gas interface cannot recede any further from the open side and the gas cluster grows within the pore network. Soon after BT, the average front position becomes almost constant over a wide range of liquid saturations (Fig. 4). This occurs because the size of interface throats is spatially random and the probability of an interface pore being invaded is the same at any distance from the product surface, as expected for IP models [34,35].

At the beginning of the CRP, the main liquid cluster (MLC) spans the entire lattice and the number of disconnected clusters (DCs) is small. During this period, evaporation takes place mainly from the MLC while DCs have a negligible contribution to the overall rate (the contribution from the DCs is marked with triangles in Fig. 4). Later, the drying rate decreases rapidly and the FRP begins. The transition between the CRP and the FRP is smooth and cannot be associated with any particular critical percolation point. It occurs before the MCD point and seems to be related to an increase in the rate of cluster formation. In fact, it appears that even during the CRP the drying rate decreases smoothly. This is consistent with experimental results by Kaviani and Mittal [29] and Van Brakel and Hertjes [30], among others.

4.1.1. Constant and falling rate periods

The drying rate is proportional to the average vapor concentration at the outlet boundary. The latter depends on the average position of the liquid–gas interface in the pore network and the area available for mass transfer. We anticipate, therefore, that the CRP lasts as long as the vapor concentration close to the outlet boundary remains constant. One may expect that pores closer to the surface would empty at higher rates, because they are subject to steeper concentration gradients and evaporate faster. However, the spanning MLC provides hydraulic connectivity across the entire pore network. Evaporation takes place from all interface throats of the cluster at rates controlled by the local concentration gradients. Therefore, pores located away form the open end empty at the same rate as pores close to it. This condition is not valid at high capillary numbers when viscous flow through the MLC produces a pressure drop which needs to be accounted for at the liquid–gas interface [31]. The conclusion that the duration of the CRP lasts as long as there is hydraulic continuity with the external surface has important implications when film flows are considered. The presence of films is expected to prolong that period, as films provide continuity in flow and transport. This is to be analyzed in a separate study.

During the early stages of the process, only a small number of DCs exist in the pore network and the MLC covers the greatest part of the outlet boundary. The drying rate remains practically constant because the area available for diffusion is limited by the presence of the MLC and gas pores become quickly saturated. During this period, evaporation takes place mainly from the MLC and the contribution of the DCs to the overall drying rate is negligible. At later times the number of DCs increases (Fig. 4) and the surface density decreases. When the number of interface throats at the perimeter of DCs becomes comparable to the number of interface throats of the MLC, the evaporation rate from DCs becomes significant. From that point on, small DCs at the outlet boundary empty at much higher rates than those away from the surface and the average evaporating front recedes again producing more space for vapor diffusion (Fig. 4). The transition between the CRP and the FRP occurs very close (but prior) to the MCD point and it is characterized by the increase in the average position of evaporating front. For a macroscopic system, and in the absence of films, therefore, we anticipate that the duration of the CRP extends close to the MCD point. This will not be the case in the presence of films, however, as the latter provide hydraulic continuity.

As noted, in these simulations we have not accounted for viscous flow, either in the form of films or in the liquid phase. The CRP would be different if we also accounted for viscous effects. Pressure gradients due to viscous flow in the liquid clusters will produce a stable evaporating front, where pores closer to the outlet boundary are preferably invaded by the gas phase over pores deeper in the pore network (gradient percolation due to concentration gradients) [31]. The effect of a stabilizing gradient on the drying rates, albeit only for gravity, is presented in Section 4.3.1. In general, a CRP is possible as long as a transport mechanism that provides hydraulic connectivity along the entire lattice exists and the open boundary remains sufficiently saturated. This mechanism can be either viscous flow through the continuous MLC or corner flow through wetting liquid films that cover the pore space walls [14,16]. Effects of liquid films will be discussed in a forthcoming publication.

Fig. 5 shows the liquid saturation and the vapor concentration at the open boundary as a function of the overall liquid saturation. During the CRP the vapor concentration at the surface decreases at a lower rate than the liquid saturation, as also shown by Suzuki and Maeda [28]. Fig. 6 shows the variation of the liquid saturation with respect to the distance from the open end. The saturation remains practically constant in the
two-phase region, where liquid and gas coexist. Prior to the MCD the continuous liquid phase is in contact with the open side at all times. After the MCD a fully dry region develops but the liquid saturation still remains constant in two-phase region. Suzuki and Maeda [28] solved the problem of drying over a partly wetted surface such as the external surface of a porous medium (Fig. 7). They showed that the mass transfer coefficient at the product surface is a function of the liquid fraction at the open boundary and that under certain conditions the drying rate remains high even at low values of the latter. However, the receding of the interface in the porous medium in a real problem produces a larger space for diffusion than considered in their approach. Therefore, their results cannot be applied directly to our problem.

4.1.2. Receding front period

When the density of the DCs becomes comparable to that of the MLC at the product surface, the FRP begins. As shown above, this occurs just before the MCD point. The MCD marks the point when the largest liquid cluster no longer spans the sample and breaks up into smaller DCs. From then on, the liquid phase disconnects from the open side and a fully dry zone with increasing thickness develops close to the open side. Because of the hindering of diffusion, the drying rate decreases very rapidly during this period. Fig. 8 shows the vapor concentration profile. The concentration remains practically constant while in the two-phase region. Initially, before the development of the completely dry zone, the vapor is saturated. At later times, after a completely dry zone has developed, a concentration gradient develops within the network. The width of the zone where the concentration gradient is appreciable increases with time as the liquid phase recedes within the pore network.

4.2. Drying in the absence of gravity ($B = 0$) but in the presence of an external diffusive layer ($d > 0$)

Consider now the problem in the absence of gravity, but in the presence of a diffusive layer of finite thickness at the open boundary (Fig. 2). Fig. 9 shows the drying curve for a pore network where the thickness of the diffusive layer is 10 or 20
times the distance between two neighboring pores. The transition between the CRP and the FRP is clear. The presence of the diffusive layer minimizes the effect of evaporation from pores located at the open boundary. The first drying period \([25]\) is negligible and the drying rate is controlled by diffusion close to the open end from the beginning of the process. However, the curves in Fig. 9 show that the number of clusters and the average front position with respect to the overall liquid saturation are the same, as in the case when \(d = 0\), as they depend solely on the percolation characteristics of the drying front.

Suzuki and Maeda \([28]\) showed that when the diffusive layer becomes thicker, the local mass transfer coefficient at the open end is constant over smaller values of the surface liquid saturation, while the CRP is longer. They also showed that for thicker diffusive layers the mass transfer coefficient exhibits a sharper decrease with decreasing surface liquid saturation (Fig. 7). Our results are consistent with their findings: Increasing the thickness of the diffusive layer decreases the absolute value of the mass transfer coefficient through the layer. The drying rate then becomes slower at the beginning of the process and the spanning MLC can sustain the evaporation rate at the open end over smaller values of the surface liquid saturation.

However, the CRP cannot last much longer than the MCD point, although this may be possible in the theoretical case when the diffusive layer thickness is much larger than the system size. This is because soon thereafter the product surface will become completely dry for the first time. Therefore, we expect that in general, the duration of the CRP can be directly associated with the MCD point.

4.3. The effect of gravity

Gravity can play an important role in drying. Buoyancy produces a two-phase zone of finite width between the bulk liquid phase and the dry zone. The structure of liquid clusters that belong to the two-phase zone is described by invasion percolation in a gradient (IPG). If the size of the pore network is much greater than the percolation correlation length, which scales as \(\sigma_f \sim B^{-v/(1+v)}\) \([24,32,33]\), the effect of gravity is negligible. Here, \(v\) is the correlation length exponent of percolation, equal to about 0.88 in 3-D.

A series of simulations for various values of the Bond number were performed on the same \(80 \times 80 \times 80\) networks. We considered two cases depending on the value of \(B\). If \(B > 0\), gravity stabilizes the percolation front and produces a microscopically rough, but macroscopically flat shape for the drying front. If \(B < 0\), gravity destabilizes the front and produces a single finger-like drying pattern that spans the network. In the numerical simulations presented in this section we ignored the presence of an external diffusive layer. As in the rest of this manuscript, the effect of liquid films was also ignored.

4.3.1. Stabilizing gradient

Fig. 10 shows phase distribution patterns at four different time steps corresponding to 80, 60, 40, and 20% overall liquid saturation, when \(B = 5.64 \times 10^{-4}\). A distinct two-phase zone develops at the early stages of the process. The thickness of the zone reaches a constant value, which does not change through the rest of the process until the BT is reached. After the BT, the gas cluster grows within the two-phase zone in a way very similar to classical IP after BT.

The drying curve for the stabilizing gradient case (Fig. 11) is at first glance very different from that in the absence of gravity (Fig. 4). The curve begins with a short FRP followed by the RFP, where drying diminishes in a smoother way. The MCD occurs very early in the process (before BT) and a clear CRP does not develop. Interface pores close to the open side are preferen-
Initially invaded over interface pores that are deeper in the network and are subject to higher buoyancy forces. Therefore, surface pores are invaded at higher rates and the MLC soon loses contact with that surface. For the same reason, the BT occurs very late in the process.

In Fig. 11 the FRP and the RFP are typical of drying in a stabilizing gradient. The number of DCs reaches an almost constant value early in the process (approximately for values of liquid saturation that are less than 0.8). The saturation profile within the two-phase zone is constant with the distance from the open end, similar with the profiles of Fig. 6. The extent of the two-phase region becomes constant very early in the process and the average front position increases almost linearly with saturation. Fig. 11 also shows the drying rate from DCs. Initially, this increases rapidly as the number of DCs increases. Soon after the MCD point, the rate from the DCs demonstrates very similar behavior to the overall drying rate. Evaporation from the DCs in the two-phase zone controls the drying process, because of the screening effect of the DCs.

4.3.2. Destabilizing gradient

Fig. 12 shows the evolution of phase distribution patterns at four time steps when $B = -1.41 \times 10^{-4}$. In this case, the gravity gradient acts to destabilize the front. Only a thin gas cluster that spans the entire network develops, early in the drying process. The BT occurs early in the process, because more distant pores are invaded at larger rates than those closer to the open end. This is opposite to the stabilizing case. When the liquid–gas interface reaches the opposite side to the open end, it cannot move further. The two-phase region close to the open side remains always saturated and the drying rate is constant (Fig. 13). The CRP in this case is due to evaporation occurring exclusively at the open boundary. This is the first drying regime identified by Le Bray and Prat [25] for capillarity-controlled drying (Fig. 1). However, in the case of a destabilizing gradient, the surface saturation remains constant at the product surface and the drying rate is also constant.

Fig. 11. Evolution of the overall drying rate, the drying rate from the isolated liquid clusters and the number of clusters with respect to the overall liquid saturation when the evaporating front is stabilized by gravity. $B = 5.64 \times 10^{-4}$, $d = 0$.

Fig. 12. Three-dimensional phase distribution patterns at 80, 60, 40, and 20% liquid saturation when the evaporating front is destabilized by gravity. Liquid clusters are shown in gray color. $B = -1.41 \times 10^{-4}$, $d = 0$. The top side is open to the ambient environment. All other sides are impermeable.

Fig. 13. Evolution of the overall drying rate, the drying rate from the isolated liquid clusters and the number of clusters with respect to the overall liquid saturation when the evaporating front is destabilized by gravity. $B = -1.41 \times 10^{-4}$, $d = 0$.

Fig. 13 shows that the CRP remains constant over a wide range of liquid saturations. Again, this is exclusively due to the constant evaporation at the open boundary. As the liquid saturation there decreases, the pore space available for diffusion increases, but the gas pores remain saturated. The process is then controlled by evaporation from the MCL, while evaporation from DCs is negligible. During this period, the drying rate decreases very smoothly as the number of DCs at the product surface increases, and the spanning MLC provides hydraulic...
connectivity across the pore network. This period corresponds to the CRP identified when capillarity controls the movement of the liquid–gas interface. Due to the destabilizing gradient, the MLC disconnects from the furthest side first, rather than at a random position of the pore network, which is the case in capillary-dominated drying. From that point on, the effect of the destabilizing gradient is negligible because the liquid phase resides mostly in liquid clusters with size smaller than the correlation length. The extent of the FRP in this process is negligible because at the MCD point the liquid saturation of the MLC at the open boundary is much greater than that of DCs.

5. Discussion

The drying curves presented show that four different drying regimes (periods) can be identified during typical drying processes:

During the first period, evaporation takes place exclusively from liquid pores at the open boundary. In the case of a capillarity-dominated evaporating front ($B = 0$), this period is very short and the drying rate exhibits a sharp decrease with increasing gas saturation. When gravity destabilizes the front ($B < 0$), this period lasts over a much wider range of liquid saturations, because the pores deeper in the pore network are preferably invaded over surface pores. The drying rate remains constant, as long as the surface liquid saturation remains unchanged. In the case of a gravity-stabilized front ($B > 0$), the pores at the surface are preferably invaded over pores deeper in the pore network and the first drying period is negligible.

The second drying period (CRP) starts after $BT$, when the liquid saturation becomes practically constant over the distance from the product surface. When capillarity controls or when gravity destabilizes the front, the drying rate remains practically constant during this period, because evaporation from the MLC at the surface dominates. In the case of a gravity-stabilized front, this period is negligible because the MCD occurs very early in the process. Either one of the two aforementioned drying periods (first or second) can be responsible for the occurrence of a CRP during drying.

The third drying period (FRP) begins when the number of DCs at the surface becomes sufficiently large and the drying rate from these clusters becomes comparable to the drying rate from the MLC. In the case of a gravity-destabilized front this period is negligible, because the number of DCs is negligible when the MLC breaks up into smaller clusters (DCs). In the case of a gravity-stabilized front this period occurs at the beginning of the process and lasts until a completely dry zone develops. Finally, during the fourth drying period (RFP) a completely dry zone develops and the process is controlled by diffusion through this zone.

Fig. 14 summarizes these findings for the three different cases. IPDG and IPSG bound capillarity-controlled drying, as they correspond to the dominance of the first and fourth periods of drying, respectively. In the case of IPDG, the liquid clusters remain in contact with the open side throughout the drying process producing a very long CRP. In the case of IPSG, the liquid clusters close to the open side evaporate early in the drying process, producing a short FRP and a long RFP.

The results obtained with our model can be qualitatively compared with the experimental results by Laurindo and Prat [10] (see Fig. 15). These authors carried out evaporation experiments in two-dimensional transparent micromodels under quasi-isothermal conditions. Fig. 16 shows the overall liquid saturation vs the dimensional time for the theoretical predictions obtained in this study. Similar trends between the predictions of this work and the experiments of Laurindo and Prat [10] are obtained. Our results also match qualitatively with the experimental findings by Kaviany and Mittal [29] and Van Brakel and Hertjees [30], among others.

In summary, the four drying regimes identified in this paper are as follows (see Fig. 17):

1. Surface evaporation regime
   Evaporation takes place at the open boundary. Only pores located at the surface are invaded and the space available for diffusion in the porous medium is negligible. During this regime, the drying rate decreases sharply until the gas...
cluster is large enough and vapor diffusion through the gas phase commences. The end of this regime occurs close to the BT point. The surface evaporation regime is negligible if the thickness of the diffusive layer over the product surface is greater than the average pore length.

2. Spanning liquid cluster evaporation regime
The evaporation rate at the open boundary is exactly balanced by the flow through the MLC. The MLC covers most of the surface and only a small number of DCs exist. Due to the spanning MLC the average position of the drying front remains practically constant. The space available for diffusion within the porous medium is limited and the gas pores become quickly saturated. During this regime the drying rate remains practically constant (CRP).

3. Disconnected liquid clusters evaporation regime
The evaporation rate at the open boundary due to DCs and the MLC becomes higher than the flow provided by the MLC there. The DCs closer to the surface empty at greater rates and the space available for diffusion increases. This regime is dominant during the FRP.

4. Receding front regime
The open surface becomes dry and diffusion takes place through the dry zone. The liquid–gas interface recedes in

the porous medium. This period begins after the MCD point.

6. Conclusions
In this paper we studied the characteristic regimes that develop during the drying of capillary porous media and particularly the constant rate and falling rate periods. Drying was simulated by a 3-D pore-network model that accounts for the effect of capillarity and buoyancy at the liquid–gas interface. The work focused on the effect of mass transfer by diffusion over an external layer and the effect of gravity on the shape of the drying curve and the relative extent of constant and the falling rate periods.

When capillarity controls the movement of the liquid–gas interface, a large liquid cluster (MLC) spans the entire network and provides hydraulic connectivity between distant liquid-occupied pores. As long as the MLC is spanning the sample and the number of interface throats is high enough to produce vapors at the product surface faster than they are drawn to the ambient environment by diffusion, the drying rate remains practically constant. When the number of interface throats of the DCs becomes comparable to those of the MLC, the CRP ends regardless of whether the MLC is still spanning or not. In general, a CRP is possible as long as a transport mechanism that provides hydraulic connectivity exists along the entire lattice and the product surface remains sufficiently saturated through this mechanism. This transport mechanism can be either viscous flow through the continuous MLC or corner flows through wetting liquid films that cover the pore space walls. The latter mechanism will be accounted in a future work.

The FRP begins when the MLC is still spanning the sample but the evaporation rate from DCs becomes comparable to the evaporation rate from the MLC close to the product surface. In this case, pores closer to the product surface, which belong to DCs are invaded at greater rates than pores located deeper in the pore space because they are subject to steeper concentration gradients. After the product surface becomes completely dry, the RFP begins during which the vapor diffuses through a dry zone of an increasing size.

In the presence of gravity the mechanisms that lead to the CRP and the FRP are more pronounced in the drying curves. For the case of gravity-stabilized front the MLC, which is responsible for the CRP, disconnects from the open boundary very early in the process, and only a short FRP and a long RFP appear in the drying curve. When the front is destabilized by gravity the MLC remains in contact with the open surface over a wider range of liquid saturations and the CRP dominates the drying curve.

We also showed that the drying rate remains constant for small values of the liquid saturation at the open boundary when the thickness of the diffusive layer over the surface is much greater than the distance between neighboring pore centers. At this limit, the transition between the CRP and the FRP is related to the MCD point.

Our findings explain the diversity of regimes identified in the experimental drying of porous materials.
References