HEAT AND MOISTURE TRANSFER IN HYGROSCOPIC POROUS MEDIA: TWO CONTRASTING ANALYSES

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ABSTRACT
The heat and mass transfer phenomena that occur in beds of ventilated hygroscopic porous media are coupled. This results in two transfer waves traversing bulks of porous medium that initially have a uniform temperature and moisture content, and that are subsequently ventilated with air that is not in thermodynamic equilibrium with the solids. The more rapidly travelling wave is known as a temperature wave and the slower wave is known as the moisture wave. Between the two waves the bed of porous medium is at its dwell state. In an Eulerian formulation of the differential equations that govern heat and mass transfer in beds of hygroscopic porous media a solution is obtained using computational fluid dynamics software. This approach has the advantage of enabling a wide range of geometries and operating conditions to be investigated. A second analysis relies on the observation that thermodynamic states of transfer waves lie on straight lines in \( \ln r - \ln p_s \) space. The Lagrangian analysis is used to investigate the effect on heat and mass transfer of the differential of the integral heat of wetting of the solids with respect to temperature. The numerical and analytical solutions are compared, and it is shown that the numerical solution captures dispersive effects arising from the finite intra-particle resistance to moisture transfer and thermal conductivity. It is observed that accounting for the differential of the integral heat of wetting of the solids with respect to temperature in the analysis has a significant effect on the predicted velocity of the temperature wave. However, this may be an artifice arising from the fact that the sorption isotherm was obtained by extrapolation to low moisture contents. It may be that sorption isotherms need to be constrained to ensure that the ratio of the differential heat of sorption to the latent heat of vaporisation of water is independent of temperature. It is shown that such isotherms do indeed lessen the effects of the integral heat of wetting on the velocity of the temperature wave. However, the velocity of the moisture transfer wave is found to be strongly dependent on the form of the isotherm.

NOMENCLATURE

- \( A_{CP} [1/\degree C] \) Constant in the Chung-Pfost isotherm equation
- \( A_i [..] \) Velocity ratio
- \( B_{CP} [..] \) Constant in the Chung-Pfost isotherm equation
- \( C_{CP} [\degree C] \) Constant in the Chung-Pfost isotherm equation
- \( A,...,D [..] \) Constants in Hunter’s isotherm equation
- \( c_a [J/(kg.\degree C)] \) Specific heat of dry air.
- \( c_s [J/(kg.\degree C)] \) Specific heat of dry grain.
- \( c_w [J/(kg.\degree C)] \) Specific heat liquid water.
- \( D_{eff} [m^2/s] \) The effective diffusion coefficient of water vapour in air.
- \( dm_a [kg] \) Mass of air that enters a region of a travelling wave.
- \( dm_s [kg] \) Mass of solids in an incremental length of a travelling wave.
- \( dx [m] \) Incremental distance along the bed of porous medium.
- \( h [J/kg] \) Specific enthalpy of moist air.
- \( h_o [J/kg] \) Specific enthalpy of dry air.
- \( h^*_o [J/kg] \) Specific enthalpy of dry air at \( T^\circ \degree C \).
- \( h_w [J/kg] \) Differential heat of wetting of solids.
- \( h^*_w [J/kg] \) Specific enthalpy of dry solid at \( T^\circ \degree C \).
- \( h^*_w [J/kg] \) Differential heat of wetting.
- \( h^*_{lw} [J/kg] \) Specific enthalpy of liquid water at \( T^\circ \degree C \).
- \( h_l [J/kg] \) Latent heat of vaporisation of water.
- \( h^*_l [J/kg] \) Latent heat of vaporisation of water at \( T^\circ \degree C \).
- \( H [J/kg] \) Specific enthalpy of moist solids.
- \( H_w [J/kg] \) Integral heat of wetting of solids, J/kg.
i ... Refers to the temperature wave \((i = 1)\) or moisture wave \((i = 2)\)

\(k\) \([1/s]\) Drying constant.

\(k_{\text{eff}}\) \([\text{W/(m.ºC)}]\) Effective thermal conductivity of a porous medium.

\(p\) \([\text{Pa}]\) Vapour pressure of water.

\(p_d\) \([\text{Pa}]\) Saturation vapour pressure of water at the dwell state.

\(p_s\) \([\text{Pa}]\) Saturation vapour pressure of water.

\(r\) \([\ldots]\) Relative humidity

\(S_1\) \([\ldots]\) Slope of the temperature transfer wave in \(\ln r - \ln p_s\) space

\(S_2\) \([\ldots]\) Slope of the moisture transfer wave in \(\ln r - \ln p_s\) space.

\(r_d\) \([\ldots]\) Relative humidity at the dwell state

\(R\) \([\text{Pa.m}^3/(\text{kg.K})]\) Gas constant.

\(t\) \([\text{s}]\) Time.

\(T\) \([\text{ºC}]\) Temperature.

\(v_a\) \([\text{m/s}]\) Component of velocity of air through the bed of porous medium.

\(v\) \([\text{m/s}]\) Velocity of air through the bed of porous medium.

\(v_{fi}\) \([\text{m/s}]\) Component of velocity of the \(i^{th}\) drying wave that traverses the bed.

\(v_{id}\) \([\text{m/s}]\) Component of velocity of a point on the wave that traverses the bed.

\(w\) \([\text{kg/kg}]\) Humidity of air.

\(W\) \([\text{kg/kg}]\) Moisture content of solid phase.

\(W_e\) \([\text{kg/kg}]\) Equilibrium moisture content.

\(W_o\) \([\text{kg/kg}]\) An empirical moisture content in Hunter’s isotherm.

\(x\) \([\text{m}]\) Distance measured from the air inlet.

**Greek symbols**

\(\varepsilon\) \([\ldots]\) Void fraction of the bed of grains

\(\varepsilon_g\) \([\ldots]\) Emissivity of grains

\(\rho_a\) \([\text{kg/m}^3]\) Density of dry air.

\(\rho_s\) \([\text{kg/m}^3]\) Density of solid phase

**INTRODUCTION**

Hygroscopic porous media are used in a wide range of industries. There is increasing interest in using beds of silica gel, for example, to remove moisture from air in air-conditioning systems such as those developed by Dai et al. [1] and Thorpe and Chen [2]. Other solid desiccants that comprise bentonite, calcium chloride and vermiculite have been used to dry air that is subsequently used to dry horticultural produce (Shanmugan and Natarajan, [3]). Stored grains, such as wheat and rice, also comprise hygroscopic media that benefit from being cooled and dried if their properties are to be preserved, hence a good understanding of the heat and mass transfer processes that occur in bulks of ventilated grain are extremely useful.

When beds of non-hygroscopic media that have an initially uniform temperature distribution are ventilated with air of a different, but constant, temperature one temperature wave traverses the bed. After the bed has been ventilated for a while a temperature wave forms, indicated by line ‘a’ in Figure 1. The solids downstream of the leading edge of the temperature wave remains unaffected by the conditions of the inlet air the porous medium remains at its initial temperature. The region upstream of the wave approaches thermal equilibrium with the ventilating air entering the bed. There is a continuous temperature wave through the bed of porous medium between the leading and trailing edges of the temperature wave. When beds of hygroscopic porous media are ventilated with moist air they usually adsorb and desorb moisture which greatly affects their thermodynamic behaviour. For example, consider a bed of hygroscopic porous medium that has been dried so that the relative humidity of the intergranular or interstitial air is low. The bed is then ventilated with air that has a high relative humidity and a lower temperature than the solids. Two waves form in this situation, as indicated by line ‘b’ in Figure 1. The wave with the higher velocity is known as a temperature wave because there is often a relatively large temperature difference across the wave, and the slower moving velocity is known as a moisture wave because there is typically a significant difference in the solids moisture content across the wave. The region between the two waves is known as the dwell state. The velocity of the temperature wave is typically two orders of magnitude greater than that of the temperature wave; in turn the speed of the temperature wave is about 3 orders of magnitude
less than the face velocity of the air through the bed of hygroscopic porous medium (Thorpe, 2001).

TWO APPROACHES TO ANALYSING HEAT AND MOISTURE TRANSFER IN HYGROSCOPIC POROUS MEDIA

The thermodynamic phenomena that occur in beds of ventilated hygroscopic porous media are analysed by formulating the partial differential equations that govern simultaneous heat and moisture transfer between the solid and fluid phases. These are prescribed by the physics of the system, and to that extent they are immutable in so far as the laws of physics are immutable. However, certain approximations can be made to their formulations that render their solutions analytically tractable. In this paper we consider two formulations and solutions of the governing equations, namely:

1) The governing equations are formulated to account for intra-particle resistance to mass transfer and thermal dispersion, and they are solved numerically.
2) Thermodynamic equilibrium is assumed between the hygroscopic porous solid and the interstitial air. The resulting equations have closed form solutions.

The two methods are quite distinct, and both are useful under different circumstances. The capability of solving the equations numerically enables designers to analyse the performance of beds of hygroscopic materials operating with arbitrary geometries and with arbitrary initial and boundary conditions. In this work we shall demonstrate how the analysis can be incorporated as a user-defined function into commercial computational fluid dynamics software that increases its flexibility even further. Numerical solutions also permit more physical phenomena to be incorporated into the governing equations. For example, Thorpe and Whitaker [4],[5] have shown that thermal equilibrium is closely approached in beds of hygroscopic porous media, but moisture equilibrium is less likely to be approached, especially when it is desired to dry, rather than simply cool a bed of porous media. The effects of intra-particle resistance to mass transfer are included in the numerical model presented in this work.

Analytical solutions to the governing equations remain extremely valuable because they enable the effects of changes to operating conditions and physical properties on the behaviour of ventilated beds of hygroscopic media to be obtained explicitly. In this work we consider a formulation of the equations that assume thermodynamic equilibrium exists between the solid and the interstitial air, and we use Hunter’s [6] method to obtain their solution. The solution of the governing equations provides useful information on the speeds of temperature and moisture fronts through beds of hygroscopic porous media, and the dwell temperature. The sorption isotherm that relates the moisture content of the interstitial air with the temperature and moisture content of the solids also plays a key rôle in the analysis. When Hunter [6] formulated the governing equations he assumed that the integral heat of wetting of porous hygroscopic porous media is not a function of temperature. An order of magnitude suggests that this may be approximately correct, particularly if one can assume that the ratio of the differential heat of sorption to latent heat of vaporisation of water is independent of temperature. This happens to be approximately the case for silica gel. If this is also true for hygroscopic media in general it must be reflected in the form of the sorption isotherm. In this work we investigate the effects of the apparent dependence of the integral heat of wetting on temperature on the behaviour of ventilated hygroscopic porous media.

FORMULATION OF THE GOVERNING EQUATIONS – AN EULERIAN APPROACH

In our numerical solution of the governing equation we adopt an Eulerian approach, that is we perform enthalpy and mass balances on a differential volume of the porous medium fixed in space.

Moisture balance

A moisture balance on a differential volume is expressed as

$$\frac{\partial (\rho_2 \varepsilon_2 W)}{\partial t} + \nabla \cdot (\rho_2 \varepsilon_2 w \mathbf{v}_s) = 0 \quad (1)$$

in which $\rho_2$ and $\varepsilon_2$ are respectively the density (dry matter basis) and the volume fraction of the solid matter in the hygroscopic porous medium, $W$ is the mean moisture content (fractional dry basis) of the solids, $\rho_a$ is the density of dry air in the interstitial air, $w$ is the absolute humidity of the air and $\varepsilon_a$ is the void fraction of the bed of grain ($= 1 - \varepsilon_a$). The mean velocity of dry air through the interstices of the grain bed is represented by $\mathbf{v}_s$. In some biological systems, such as bulk stored grains, the solid substrate can be consumed by fungi hence $\rho_2 \varepsilon_2$ and $\varepsilon_a$ are not necessarily constant, but in this study we assume that these biological activities are negligible.

A moisture balance on the solid phase can be expressed in the form

$$\frac{\partial W}{\partial t} = -k (W - W_s) \quad (2)$$

in which $k$ is the ubiquitous drying constant and $W_s$ is the moisture content of the solid phase in thermodynamic equilibrium with the interstitial air.

Enthalpy balance

It has been noted above that the air and the grains are in thermal equilibrium and the enthalpy balance on the air and solids is written as

$$\frac{\partial (\rho_a \varepsilon_a H)}{\partial t} + \nabla \cdot (\rho_a \varepsilon_a h \mathbf{v}_s) = k_{ef} \nabla^2 T \quad (3)$$

in which $H$ is the specific enthalpy of the moist solids phase and $h$ is the specific enthalpy of the moist interstitial air. The
thermal conductivity, $k_{eff}$, of the porous medium is taken to be isotropic.

The specific enthalpy, $H$, of the moist solids is defined by

$$H = h_s + c_s \left( T - T^o \right) + H_m + W \left( k_m + c_m \left( T - T^o \right) \right)$$  \hspace{1cm} (4)

in which the subscripts ‘s’ and ‘w’ refer to the solid substrate and moisture respectively. $h^o_s$ and $h^o_w$ are standard enthalpies determined at some standard temperature $T^o$, and these do not have to be calculated because when enthalpy conservation equations are balanced they do not figure in the result. This helps to serve as a check on the algebra.

$H_W$ is the integral heat of wetting of the solid phase expressed in J/kg of dry solid. The integral heat of wetting becomes increasingly negative as the moisture content increases and this implies that the internal energy of the solid decreases as it becomes wetter. The specific heats of dry solid and liquid water are $c_s$ and $c_w$ respectively.

The enthalpy of water vapour, $h_v$, is given by

$$h_v = h^o_v + c_v \left( T - T^o \right) + h_i$$  \hspace{1cm} (5)

where $h_i$ is the latent heat of vaporisation of liquid water at temperature $T$.

Expanding equation 3 results in

$$\rho \epsilon_s \frac{\partial H}{\partial t} + \frac{(\rho \epsilon_s h)}{\partial t} + \nabla \cdot (\rho \epsilon_s h \cdot \mathbf{v}) = k_{eff} \nabla^2 T$$  \hspace{1cm} (6)

Equation 6 can be expressed in terms of physical properties by noting the following relationships

$$\frac{\partial H}{\partial t} = \frac{\partial H}{\partial W} \frac{\partial W}{\partial t} + \frac{\partial H}{\partial T} \frac{\partial T}{\partial t}$$  \hspace{1cm} (7)

$$\frac{\partial H}{\partial W} = \frac{\partial H}{\partial W^o} + h^o_w + c_w \left( T - T^o \right)$$  \hspace{1cm} (8)

$$\frac{\partial H}{\partial T} = c_s + \frac{\partial H}{\partial T^o} + c_s W$$  \hspace{1cm} (9)

$$\frac{\partial h^o_s}{\partial t} = c_s \frac{\partial T}{\partial t} + \frac{\partial h^o_s}{\partial T} \frac{\partial T}{\partial t}$$  \hspace{1cm} (10)

$$\nabla h^o_v = c_v \nabla T + \frac{\partial h^o_v}{\partial T} \nabla T$$  \hspace{1cm} (11)

$$\frac{\partial h^o_v}{\partial t} = c_a \frac{\partial T}{\partial t}$$  \hspace{1cm} (12)

$$\nabla h^o_v = c_a \nabla T$$  \hspace{1cm} (13)

We also note that the enthalpy of the interstitial air is the sum of the enthalpies of dry air and water vapour, hence

$$\rho \epsilon_a h = \rho \epsilon_a \left( h^o_v + c_v \left( T - T^o \right) + w \left( h^o_v + c_v \left( T - T^o \right) + h_i \right) \right)$$  \hspace{1cm} (14)

Making use of equations 7 to 14 and inserting them into equation 6 enables one to write

$$\rho \epsilon_s \left( c_s + \frac{\partial H}{\partial T} + c_s W \right) \frac{\partial T}{\partial t} + \rho \epsilon_s \left( \frac{\partial H}{\partial W} + h^o_w + c_w \left( T - T^o \right) \right) \frac{\partial W}{\partial t}$$

$$- \rho \epsilon_s \left( h^o_w + c_w \left( T - T^o \right) + h_i \right) \frac{\partial W}{\partial t} + \rho \epsilon_s c_s \frac{\partial T}{\partial t}$$

$$+ \rho \epsilon_v \frac{\partial h^o_v}{\partial t} \frac{\partial T}{\partial t} + \rho \epsilon_v \frac{\partial h^o_v}{\partial T} \frac{\partial T}{\partial t}$$

$$+ \rho \epsilon_v \frac{\partial h^o_v}{\partial t} \frac{\partial h^o_v}{\partial T} \frac{\partial T}{\partial t}$$

Cancelling out the repeated factors in equation 15 leads to

$$\rho \epsilon_s \left( c_s + \frac{\partial H}{\partial T} + c_s W \right) \frac{\partial T}{\partial t} + \rho \epsilon_s \left( \frac{\partial H}{\partial W} - h_i \right) \frac{\partial W}{\partial t}$$

$$+ \rho \epsilon_v \frac{\partial h^o_v}{\partial t} \frac{\partial T}{\partial t} + \rho \epsilon_v \frac{\partial h^o_v}{\partial T} \frac{\partial T}{\partial t}$$

$$+ \rho \epsilon_v \frac{\partial h^o_v}{\partial t} \frac{\partial h^o_v}{\partial T} \frac{\partial T}{\partial t}$$

This equation can be further simplified by noting that the differential heat of sorption of water on the solids, $h_s$, is defined as

$$h_s = h^o_v - h_v$$  \hspace{1cm} (17)

in which $h_v$ is the differential heat of wetting of the solids, a negative quantity. The heat of sorption is the energy that must be supplied to one kg of water bound to the solid substrate to convert it to the vapour form. The differential heat of wetting of hygroscopic solids is the decrease in energy a mass of grains when one kg of water is added to it at a given moisture content. The reason the energy of the dry solids is reduced in the wetting process is that they have the capacity to perform work on water molecules by attracting them to their surfaces – as the grains become more moist this potential energy gets less and this is reflected in the enthalpy of the grains.

The integral heat of wetting, $H_W$, is defined by

$$H_W = \int \frac{h_v dW}{\theta^o}$$  \hspace{1cm} (18)

and this is the total reduction in surface energy of the solids when they adsorb moisture. The latent heat of vapourisation of
FORMULATION OF THE GOVERNING EQUATIONS – A LAGRANGIAN APPROACH

Our objective is to obtain expressions for the speeds, \( v_{f,1} \) and \( v_{f,2} \), of the temperature and moisture fronts respectively from an equation of the form

\[ v_{f,i} = A_i v_e \]

in which \( v_e \) is the average velocity component of the interstitial air as it flows through the bed of porous medium and \( A_i \) are known as the velocity ratios that depend on the local thermodynamic state of the bed of porous medium. We also wish to calculate the temperature, interstitial humidity and the moisture content of the solid phase at the dwell state.

A Lagrangian formulation of the heat and mass balance equations can be used to obtain explicit equations for the speeds of moisture and temperature fronts through beds of hygroscopic porous media. The basic idea is to consider points on the transfer waves that remain at constant thermodynamic states on the waves as they traverse the bed. This removes the necessity to consider transient equations, and the resulting enthalpy and mass balance equations collapse into one simple equation that has two unknowns. The sorption isotherm equation that relates the thermodynamic states of interstitial air and solid phase is used to derive an equation that contains the two unknowns, and the resulting simultaneous equations can be solved explicitly. The method was first presented Hunter [6] and we shall repeat the key features of his analysis, but include the apparent effect of the temperature dependence of the integral heat of wetting of the solid phase on the overall performance of a ventilated bed of hygroscopic porous medium.

To illustrate the idea consider two adjacent differential longitudinal elements in the bed, each of length \( dx \). At a time \( t \) the enthalpies of the solid phase and air at the trailing edge of a transfer wave are respectively \( H + dH \) and \( h + dh \); the corresponding moisture contents of the solid phase and air are similarly notated as shown in Figure 2. The corresponding enthalpies at the leading edge of the wave are \( H \) and \( h \) and those at the leading edge of the adjacent, downstream element, are \( H - dH \) and \( h - dh \).

![Figure 2. Three points on a transfer wave traversing a bed of porous hygroscopic medium](image)

During the time \( \Delta t \) it takes for the upstream element to travel a distance \( \Delta x \) the moisture content of the solids in the downstream element increases from \( W - dW/2 \) to \( W + dW/2 \), i.e. by \( dW \). During the same time the moisture content of the air entering the downstream element increases from \( w \) to \( w + dw \) so its mean value is \( w + dw/2 \), and the average value leaving the element is \( w - dw/2 \). A mass balance on the...
downstream element of unit cross-sectional area normal to the
air flow is therefore expressed as

\[ \rho_s (v_a - v_r) (w + dw/2) \Delta t \]

\[ = \rho_s (v_a - v_r) (w - dw/2) \Delta t + \rho_v \cdot \Delta t \]

(26)

The quantity \( \rho_s (v_a - v_r) \) is the mass rate at which dry air enters the element and it accounts for the fact that the element itself has a velocity component \( v_r \), and \( v_a - v_r \) is the relative velocity of the moving wave and the air.

Equation 26 may be expressed in a form similar to that presented by Hunter [6], namely

\[ dm_dw = dm_dW \]

(27)

where \( dm_dw \) is the mass of air flowing into the element during the time it has moved a distance \( dx \) and the corresponding mass of solids in the element is \( dm_s \). Analogous reasoning leads to the enthalpy balance being expressed as

\[ dm_s dh = dm_s dH \]

(28)

Equations 27 and 28 were reported by Griffith [10] in his pioneering studies of cooling and drying systems for bulk stored grains, and they formed the basis of an analysis based on the method of characteristics presented by Sutherland et al. [11].

Although it is somewhat tedious we shall expand equations 4 and 14 to obtain expressions for \( dh \) and \( dH \) in terms of system properties and thermodynamic variables.

The differential enthalpy balance on the moist solids is

\[ dH = c_{s}dT + W \left( h_s + c_w (T + dT - T^0) \right) \]

\[ + \left( \frac{\partial}{\partial W} \int_{w_0}^{w} (h_s - h_r) dW \right) dT \]

\[ + \left( h_s + c_w (T - T^0) \right) dW + h_r - h_i \]

and the differential energy balance on the interstitial air is

\[ dh = c_{a}dT + w_c dT + w \frac{dh_c}{dT} dT \]

\[ + \left( h_s + h_a (T - T^0) + h_r + \frac{dh_c}{dT} (T - T^0) \right) dw \]

(30)

From equations 27 and 28 we easily obtain

\[ \frac{dh}{dw} = \frac{dH}{dW} \]

(31)

Hence, dividing equation 29 by \( dW \) and equation 30 by \( dw \) and noting that at the temperature \( T \) the latent heat of vaporisation of free water is

\[ h_r = h_r^0 + \frac{dh_r}{dT} (T - T^0) \]

(32)

and that

\[ \frac{\partial}{\partial W} \int_{w_0}^{w} (h_s - h_r) dW = h_i - h_s \]

(33)

we obtain the following conservation equation

\[ C'_a \frac{dT}{dw} + C'_w \frac{dT}{dW} + h_i = 0 \]

(34)

in which

\[ C'_a = c_a + wc_a + w \frac{dh_c}{dT} \]

(35)

and

\[ C'_w = c_w + Wc_w + \frac{dH_u}{dT} \]

(36)

Note that equation 36 contains the differential of the integral heat of wetting of the solid phase with respect to temperature, a term to be investigated as part of this study.

**Calculating the velocity ratios**

Equation 34 has two unknowns, \( dT/dw \) and \( dT/dW \). To evaluate these unknowns we require a second equation and Hunter [6] shows that this can be derived from the sorption isotherm and he obtains

\[ \frac{dw}{dT} = \frac{dW}{dw} \left( \frac{dw}{dT} - \frac{wh_c (0.622 + w)}{RT^2 (0.622)} \right) \]

(37)

which can be used to eliminate \( dT/dW \) from equation 34 with the result

\[ \left( \frac{h_i \frac{dw}{dT}}{C'_a} \right)^2 + \left( 1 - \frac{C'_w}{C'_a} \right) \frac{dw}{dT} - \frac{0.622 + w}{0.622} \frac{wh_c}{C'_a} \]

\[ \frac{0.622 + w}{0.622} \frac{wh_c}{C'_a} RT^2 = 0 \]

(38)

This quadratic equation provides two values of \( dw/dT \), one of which applies to the temperature wave and the other to the moisture wave and they can be used to calculate the respective velocity ratios from the equation.
Calculating the dwell state
The dwell state is calculated by recognising that the loci of points on the transfer waves lie approximately on a straight line in \( \ln r - \ln p_s \) space. We can calculate the values of \( r \) and \( p_s \) at the air inlet and in the porous medium at its initial state, and if we know the slopes of the lines along the transfer waves the intersection of the lines is at the dwell state. Since the slope, \( S \), is given by

\[
S = \frac{p_s}{r} \frac{\partial r}{\partial p_s}
\]

(39)

it can be shown that

\[
S_i = \frac{0.622 \times 10^{-6} \times T}{0.622 + w} \frac{RT}{h_v} \frac{dW}{dT} - 1
\]

(40)

The saturation vapour pressure, \( p_{s_i} \), at the dwell state is given by

\[
p_{s_i} = \left( \frac{r_i}{p_i} \right)^{\frac{1}{n - s_i}}
\]

(41)

and the corresponding value of the relative humidity, \( r_{s_i} \), of the interstitial air is

\[
r_{s_i} = r_i \left( \frac{p_{s_i}}{p_i} \right)^{1/n - s_i}
\]

(42)

Hunter [6] demonstrates how approximate explicit equations may be derived for the velocity ratios, \( A_i \), and the slopes, \( S_i \), of the transfer waves in \( \ln r - \ln p_s \) space and they have been used in this work.

THE SYSTEM INVESTIGATED

Physical properties
Two sorption isotherms have been used to relate the relative humidity, \( r \), of the interstitial air and the temperature, \( T \), and moisture content, \( W \), of the solid phase. One of the most widely used isotherms is that proffered by Chung and Pfost [12], namely

\[
r = \exp \left( -\frac{A_{CP} W}{T + C_{CP}} \right) \exp \left( -B_{CP} W \right)
\]

(43)

in which \( A_{CP}, B_{CP} \) and \( C_{CP} \) are empirical constants that assume the values of 921.65, 18.08 and 112.35 respectively when the porous medium is Durum wheat. Hunter [13] shows how sorption isotherms can be used to derive the differential heat of sorption of moisture on the solids, and Thorpe [14] provides analytical expressions for the integral heat of wetting, \( H_W \), and its derivative with respect to temperature, \( \partial H_W / \partial T \).

A second isotherm explored in this work is the one suggested by Hunter [13], namely

\[
r = \left( \frac{p_s}{p_i} \right)^{\frac{h_v}{h_i} - 1}
\]

(44)

in which \( p_o \) is a material-specific empirical constant and the saturation pressure of water vapour, \( p_s \), is calculated using Hunter’s (1987) formula, namely,

\[
p_s = \frac{6 \times 10^{25}}{(T + 273.15)} \exp \left( -\frac{6800}{T + 273.15} \right)
\]

(45)

A feature of Hunter’s isotherm is that ratio \( h_v / h_i \) is deemed to be independent of the moisture content, \( W \), of the solids and it is calculated from

\[
\frac{h_v}{h_i} = 1 + \frac{A \ln(W/W_o)^{\alpha} C \ln(W/W_o)}{1 - (W/W_o)^{\alpha}}
\]

(46)

in which \( A, B, C, D \) and \( \alpha \) are solid-specific empirical constants. \( W_o \) is calculated from

\[
W_o = \left( \frac{B_t}{D^t} \right)^{\frac{1}{(C - A)}}
\]

(47)

Whilst it may be appropriate that \( h_v / h_i \) is independent of the moisture content, \( W \), there is no accurate explicit reversion formula that enables the moisture content, \( W \), of the solids to be calculated from \( r \) and \( T \), and in this work it has been reverted numerically. Thorpe et al. [15] have shown that the integral heat of wetting, \( H_W \), can be expressed in terms of infinite series and the tric-gamma function (Abromowitz and Stegun, [18]). To simplify the evaluation of these function Thorpe et al. [15] have expressed \( H_W \) as fourth order polynomials in \( W \). Other physical properties used in the calculations are given in Table I.

A bulk of ventilated wheat is chosen to compare the two contrasting analyses of heat and moisture transfer in beds of hygroscopic porous media. This is a technologically important porous medium because food grains must be stored for several months, and if suitable storage conditions are not maintained the grains may be attacked by moulds, insects and their quality may deteriorate. The conditions chosen to study the effects of ventilation on conditions within a bed of wheat are as follows:

Initial moisture content, \( W \), of wheat: 10% dry basis
Initial temperature of the wheat: 30°C
Humidity of air entering the bed of wheat: 0.006 kg/kg
Temperature of air entering grain: 10°C
Superficial velocity of the air: 0.01088 m/s

Table I. The physical properties of the system investigated

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_a$</td>
<td>1017 J/(kg.°C)</td>
</tr>
<tr>
<td>$c_w$</td>
<td>4187 J/(kg.°C)</td>
</tr>
<tr>
<td>$c_s$</td>
<td>1298 J/(kg.°C)</td>
</tr>
<tr>
<td>$\rho_a$</td>
<td>1.169 kg/m³</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>1172.9 kg/m³</td>
</tr>
<tr>
<td>$R$</td>
<td>461.92 Pa.m³/(kg.K)</td>
</tr>
<tr>
<td>$\varepsilon_a$</td>
<td>0.41</td>
</tr>
<tr>
<td>$\varepsilon_s$</td>
<td>0.59</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Numerical solution

The passage of two transfer waves after an elapsed time of $3.22 \times 10^4$ s can be discerned from Figures 3 and 4. Figure 3 shows that the leading edge of the temperature wave that is at the initial temperature of the grain, namely 30°C, is just about to be expelled from the bed. The temperature varies continuously along the wave and the slower moving trailing edge of the wave is at a dwell temperature of about 18°C. Dispersive effects arising from the finite intra-particle mass transfer resistance and thermal conductivity result in the wave being smeared. This is also evident in the moisture wave, the leading edge of which clearly travels at a lower velocity than that of the trailing edge of the temperature wave. The region between the moisture and temperature waves, the dwell state is clearly delineated. Because the trailing edge of the moisture transfer wave has such a low velocity it cannot be discerned after the relatively small elapsed time, and because dispersion has smeared the wave. The corresponding moisture contents of the porous medium are shown in Figure 4. It can be seen that moisture content at the leading edge of the moisture wave is 0.1, the initial moisture content of the material. The moisture content at the dwell state is about 0.0924 and the temperature of the solids at the air inlet is 0.163. It can be seen that there is a significant change in moisture content across the moisture wave, hence its appellation. It is worthwhile noting that the solids at the air inlet have not attained their equilibrium moisture content of 0.1916 because of the finite resistance to moisture content within the grain kernels.

After a prolonged period of time, namely $1.77 \times 10^6$ s, the temperature wave has been completely expelled from the bed and the solids have approached thermodynamic equilibrium with the incoming air, as can be observed from Figures 5 and 6.

Figures 5 and 6 suggest that the analytical and numerical solutions predict very similar velocities of the moisture wave.

Effects of the sorption isotherm

In this work equations 39, 41 and 42 were used to investigate the effects of the sorption isotherm on the behaviour of ventilated beds of hygroscopic porous media. Four cases have been studies, namely:

- Use of the Chung-Pfost isotherm with $\frac{\partial H_w}{\partial T} = 0$
- Use of the Chung-Pfost isotherm with $\frac{\partial H_w}{\partial T} \neq 0$
- Use of Hunter’s isotherm with $\frac{\partial H_w}{\partial T} = 0$
- Use of Hunter’s isotherm with $\frac{\partial H_w}{\partial T} \neq 0$

The trailing edge of the moisture wave has penetrated the bed by about 0.2m.

Results from the analytical solution of the thermal energy and moisture conservation equations are shown in Table II, and they are superimposed on the numerical solutions sown in Figure 3, 4, 5 and 6. The analytical and numerical solutions do not account for $\frac{\partial H_w}{\partial T}$. It can be seen from Figures 3 and 4 that both analyses predict similar celerities of the temperature wave, but that the numerical solution manifests the effects resulting from mass and thermal dispersion. The analytical solution assumes thermodynamic equilibrium between the phases and this is results in the moisture content of the solids having a higher value at the air inlet compared with the numerical solution for the reason alluded to above.
Figure 4. The moisture content profile along a bed of ventilated porous medium. It can be seen that the moisture content at the exit of the bed remains at its initial value of 0.1, whereas the temperature in the dwell region is about 0.095. The moisture content of the solids at the air inlet is 0.1525 which is lower than its equilibrium moisture content of 0.192 because of the finite resistance to mass transfer within the particles.

Figure 5. The temperature profiles in a bed of ventilated porous medium after an elapsed time of $1.772 \times 10^4$ seconds. The solids in the first 0.2 m of the bed are in thermodynamic equilibrium with the air used for ventilation, and the solids near the exit of the bed are close to the dwell temperature of about 18ºC.

Figure 6. The moisture content profile in a bed of ventilated porous medium after an elapsed time of $1.772 \times 10^4$ seconds. The solids in the first 0.2 m of the bed have a moisture content of 0.192 and they are in thermodynamic equilibrium with the air used.

A key feature of the results is that when the Chung-Pfost [12] isotherm is adopted the effect of including the effects of $\frac{\partial H_w}{\partial T}$ is to slow the predicted celerity of the temperature wave. This is because $\frac{\partial H_w}{\partial T}$ calculated from the sorption isotherm to be about 800 J/kg of water adsorbed as pointed out by Thorpe [14]. It is highly unlikely that this is the case because measurements made on hygroscopic porous media suggest that differential heat of sorption, $h_w$, is independent, or a very weak function, of the moisture content of the solids. One may make a *prima facie* estimate of $\frac{\partial H_w}{\partial T}$ by reasoning that

$$\frac{\partial H_w}{\partial T} = \frac{\partial}{\partial T} \int_0^{1000} \left( 1 - \frac{h}{h_i} \right) dW = O(1000 \times 0.1 \times 0.1) = O(10)$$

in which 1000 is the order of magnitude of the first derivative of the latent heat of vaporisation of water with respect to temperature, the second term, 0.1, arises from $1 - h_i/h_i$, and the final 0.1 is the integral of $dW$, and it is on the order of 0.1. This clearly about two orders of magnitude less than the value calculated using the Chung-Pfost [12] isotherm. When Hunter’s isotherm, equation 46 and 47, is used it is found that $\frac{\partial H_w}{\partial T} = 87$. This is a relatively small fraction of the specific heat of the moist solid phase which is about 1700. The results are shown in Table II.
Table II. The effects of including $\partial H_w / \partial T$ in the conservation equation on the dwell state and velocity ratios

<table>
<thead>
<tr>
<th>Variable</th>
<th>Chung-Pfost (1967) isotherm</th>
<th>Hunter (1987) isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W$ at the air inlet</td>
<td>0.1916</td>
<td>0.1916</td>
</tr>
<tr>
<td>$W$ at the dwell state</td>
<td>0.0958</td>
<td>0.0943</td>
</tr>
<tr>
<td>$T$ at the dwell state</td>
<td>17.99°C</td>
<td>18.24°C</td>
</tr>
<tr>
<td>$w$ at the dwell state</td>
<td>$3.644 \times 10^{-3}$</td>
<td>$3.588 \times 10^{-3}$</td>
</tr>
<tr>
<td>$A_1$ leading edge of temperature wave</td>
<td>$1.149 \times 10^{-3}$</td>
<td>$8.493 \times 10^{-4}$</td>
</tr>
<tr>
<td>$A_1$ trailing edge of temperature wave</td>
<td>$7.463 \times 10^{-4}$</td>
<td>$5.098 \times 10^{-4}$</td>
</tr>
<tr>
<td>$A_2$ leading edge of moisture wave</td>
<td>$3.328 \times 10^{-5}$</td>
<td>$3.375 \times 10^{-5}$</td>
</tr>
<tr>
<td>$A_2$ trailing edge of moisture wave</td>
<td>$8.856 \times 10^{-6}$</td>
<td>$8.856 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

A second feature of the results is that the velocity ratios of the temperature wave are calculated to be relatively independent of the form of the isotherm used (when the effects of $\partial H_w / \partial T$ are ignored). However, the velocity ratios of the moisture wave are strongly dependent on the form of the sorption isotherm although they are relatively insensitive to inclusion of $\partial H_w / \partial T$ in the analysis. When the Chung-Pfost [12] isotherm is used the velocity ratio of the trailing edge of the moisture wave is $8.856 \times 10^{-6}$, whereas when Hunter’s isotherm is used it is estimated to be $2.900 \times 10^{-5}$, a factor of about 3.4. This may be technologically significant. It is clear that the proper selection of sorption isotherms is essential in the modelling of heat and mass transfer phenomena that occur in beds of hygroscopic porous media. Deciding how to make a proper choice remains a research question. The analysis presented in this work enables the effect of a range of sorption isotherms on the performance of ventilated beds of porous hygroscopic media, and this may guide searches for improved materials.

CONCLUSIONS

Hygroscopic porous media are found naturally in the form of agricultural produce and in the form of minerals, and hygroscopic media, such as silica gel, are manufactured. Technological applications demand that the behaviour of bed of ventilated beds of porous media are accurately modelled. This entails formulating equations for the transport of energy and moisture within the interstitial air that are coupled with equations that govern energy and moisture conservation of the solids. The coupling is achieved through sorption isotherms. In this work the equations have been solved numerically using proprietary computational fluid dynamics software. This entails supplying user-defined functions that account for the source terms in the mass and energy conservation equations. A second approach has been to use analytical solutions of the equations originally developed by Hunter (1988). As one might expect, agreement between the numerical and analytical solutions is close, but the former are able to account for finite mass transfer resistance between the solids and the interstitial air. The analysis highlights that the differential of the heat of wetting of porous media with respect to temperature has the apparent effect of slowing the passage of temperature waves through beds of ventilated porous media. This is likely to be an artefact of the empirical correlations used to develop sorption isotherms. The effect was not observed when a sorption isotherm was used that constrains the ratio of the differential heat of sorption to the latent heat of vaporisation of water to be a function only of the moisture content of the solids. The form of the sorption isotherm also has a profound effect on the speed of moisture waves through bed of ventilated hygroscopic porous media. An examination of the factors that affect the choice of materials with given sorption isotherms is a worthy research question.

REFERENCES


