Predicting the Steam Drying Behavior of Diverse Low Rank Coals

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Abstract

There are three types of moisture in very low rank coals: (i) Monolayer moisture fully interacts with metal carboxylates, carboxylic acids, and phenolic hydroxyls in the coal structure via ionic bonding complexes and hydrogen bonds; (ii) Multilayer moisture forms a hydrogen bonded layer over monolayer moisture via long-range interactions with dissolved cations; and (iii) Bulk moisture is simply water that volumetrically fills the bulk of the pore voidage, without chemical interactions with coal components. Our drying model explicitly accounts for these three forms, as a basis to predict the distinctive drying behavior and energy requirements of individual low rank coal samples. The mass loadings of the moisture forms are estimated from a database of equilibrium moisture contents that we correlated to parameters derived from a coal's proximate and ultimate analyses. The analysis is validated with laboratory tests on steam drying in autoclaves and a fluidized bed that cover ranges of steam pressures and temperatures for an assortment of Australian brown coals. Then the analysis is used to determine which forms of moisture affect drying times the most.

The drying time is not solely a function of the total moisture content of the coal. For some selections of coal samples, drying time will be proportional to total moisture, and for other selections, there will be exceptions. One key aspect is whether or not the target moisture level requires removal of any monolayer moisture at all. Coals with abundant bulk and multilayer moisture can achieve targets of, say, 10 % residual moisture by vaporizing only a portion of the multilayer moisture. Consequently, their drying times and enthalpy requirements will be relatively modest. But coals with little bulk moisture and relatively abundant monolayer moisture will require relatively long drying times simply because monolayer moisture is always released much more slowly than multilayer moisture. Hence, the distribution of the three forms of moisture in any particular coal sample is an important determining factor for both drying time and enthalpy requirements.

Introduction

As explained in more detail elsewhere [1], there are three types of moisture in brown coals: (i) Monolayer moisture fully interacts with functional groups in the coal structure via hydrogen bonds and ionic bonding complexes; (ii) Multilayer moisture forms a hydrogen bonded layer over monolayer moisture via long-range interactions; and (iii) Bulk moisture is simply water that volumetrically fills the bulk of the pore voidage, without chemical interactions with coal components. Monolayer and multilayer moisture are primarily stabilized by three functional groups in the coal: Metal carboxylates, carboxylic acids, and phenolic hydroxyls. Moisture on metal carboxylates is ionically bound and therefore immobile, whereas the moisture on carboxylic acids and phenolic hydroxyls is hydrogen bonded and fully mobile, as are the acidic protons and the hydroxyl protons from the coal structure. Within brown coal, a thermochemical equilibrium determines the concentrations of metal carboxylates, carboxylic acids, and the concentrations of metallic cations dissolved in the monolayer and multilayer moisture. This equilibrium may be affected by the pH of the bulk moisture. Bulk moisture acts as a reservoir that responds to changes in the proportions of metal carboxylates and carboxylic acids.

During drying, the three forms of moisture are released sequentially. Bulk moisture is released via evaporation and requires only the normal enthalpy of vaporization. Multilayer moisture is released by supplementing the enthalpy of vaporization with the free energy of formation of the hydrogen bonded multilayer. Monolayer moisture is released by supplementing the enthalpy of vaporization with the energy requirement to break the hydrogen bonds to phenolic hydroxyls and carboxylic acids, and to convert the metal carboxylates into an organic crosslink plus a free metallic acid. During drying at temperatures above about 150°C, metal carboxylates, carboxylic acids, and phenolic hydroxyls spontaneously decompose into CO_2, H_2O, and organic crosslinks within coal macromolecules. At temperatures above about 250°C, these decompositions become extensive enough to affect the thermochemical equilibrium that determines the concentration of cations, carboxylic acids and carboxylates dissolved in multi- and monolayer moisture.

Unfortunately, we were unable to locate a single quantitative analysis of brown coal drying that explicitly recognized the different forms of moisture, and their distinctive drying behavior. Bulk moisture vaporization is the only evaporation mechanism in all the available models. In contrast, we regard these different forms of moisture as an essential aspect of our proposed analysis, without which there is little hope of describing the distinctive drying behavior of individual brown coal samples. This paper introduces the elements of our drying analysis, and validates the model predictions in comparisons with several reported drying histories from lab-scale steam drying experiments.

The Drying Analysis

The reaction system is a single, spherical particle of brown coal with specified proximate and ultimate analyses and particle diameter. Initially, the particle holds three forms of moisture: (1) Monolayer moisture that is chemically bound to carboyxlates, carboxylic acids, and phenolic hydroxyls that are exposed in internal pore walls; (2) Multilayer moisture that is weakly connected by hydrogen bonds and weak ionic interactions to monolayer moisture; and (3) Bulk moisture that is acidified by dissolved cations and that volumetrically fills the coal's internal pore system, without interactions with the pore walls. Initially the particle is at uniform temperature, and the mass fractions of the three forms of moisture are specified.

At some specified time, the particle is injected into a drying environment with specified uniform temperature, pressure, and steam concentration. The description of the drying environment is sufficient to describe the external heat flux to the particle. For example, in a fluidized bed dryer, sufficient information would need to be provided to evaluate an overall heat transfer coefficient. The external heat flux would then be evaluated as the product of the heat transfer coefficient and the instantaneous

temperature difference between the particle and fluidizing gas.

As seen in Fig. 1, the drying process then proceeds through three stages: (1) Preheating; (2) Bulk Vaporization; and (3) Single-Layer Drying under chemical reaction control. Preheating simply increases the particle temperature while the particle absorbs the external heat flux without releasing any moisture. Temperature profiles are established from the external surface to the center while the external heat flux is conducted through the coal and moisture. The preheating stage lasts as long as necessary to bring the external surface to the boiling point, where the first bulk moisture begins to vaporize. As soon as the external surface is heated to the boiling point for the specified drying conditions, a bulk moisture vaporization front starts to move toward the center. The conduction flux into the front from the exterior shell provides sufficient energy to vaporize only the bulk moisture, and to continue to conduct energy toward the center. The net conduction flux across the vaporization front equals the latent heat of vaporization, so the front remains at the boiling point while it moves toward the center.

The exterior shell beyond the vaporization front continues to conduct the external heat flux, but at a slower rate due to the replacement of bulk water by steam within the internal pore system, which lowers the thermal conductivity. We propose that this escaping steam in the shell around the bulk vaporization front prevents multilayer moisture from evaporating, even while the temperature through the outer layer continues to increase via heat conduction. Only after the bulk vaporization front reaches the particle center and vanishes does multilayer moisture start to evaporate.

At this point, the mass fraction of multilayer moisture is fixed at the initial value throughout the particle. It then diminishes at the fastest rate at the external surface where the local temperature is hotter. Eventually, the concentration of multilayer moisture vanishes from the external surface, which leaves only monolayer moisture. This region expands into an exterior shell due to the continuous conduction of the external heat flux. So there are now two domains, a core that contains a concentration profile of multilayer moisture on a uniform mass fraction of monolayer moisture and a shell that contains a profile of monolayer moisture. Since both regions have concentration profiles determined by the decomposition rates of bound moisture, this stage is labeled as the Reaction Control Stage in Fig. 1.

According to this phenomenology, bulk moisture is released by an ordinary vaporization process that moves in a front from the external surface to the center. This front delineates a core that contains the initial level of bulk moisture and an exterior shell that has no bulk moisture whatsoever. The vaporization front remains at the boiling point while it moves to the center. Once it reaches the center and vanishes, multilayer moisture begins to vaporize wherever the particle temperature is hot enough to overcome its enhanced enthalpy of vaporization. This vaporization will be biased toward the external particle surface, where the temperature is hottest, while the drying endotherm suppresses radial temperature gradients.

When all the multilayer moisture has been released from the external surface, an exterior shell that contains only monolayer moisture forms. To the left of this boundary, the mass fraction of multilayer moisture increases for progressively smaller radial positions, and the mass fraction of monolayer moisture remains at its initial value. On this boundary, there is no multilayer moisture but the mass fraction of monolayer moisture remains at the initial level; and further to the right, the amount of monolayer moisture diminishes for progressively greater radial positions. In this configuration, monolayer moisture persists at the initial level until all multilayer and bulk moisture have been released from a given position. Similarly, monolayer and multilayer moisture persist at their initial levels until all bulk moisture has been released from the entire particle, due to an equilibration of the mono- and multilayer moisture with the escaping steam from the bulk vaporization front. In this way, this analysis depicts the sequential elimination of the three forms of moisture.

The release rates of multi- and monolayer moisture are in Arrhenius form with a power-law order in temperature of 1.5 and an apparent activation energy of 1 kcal/mole, which are within the range of values
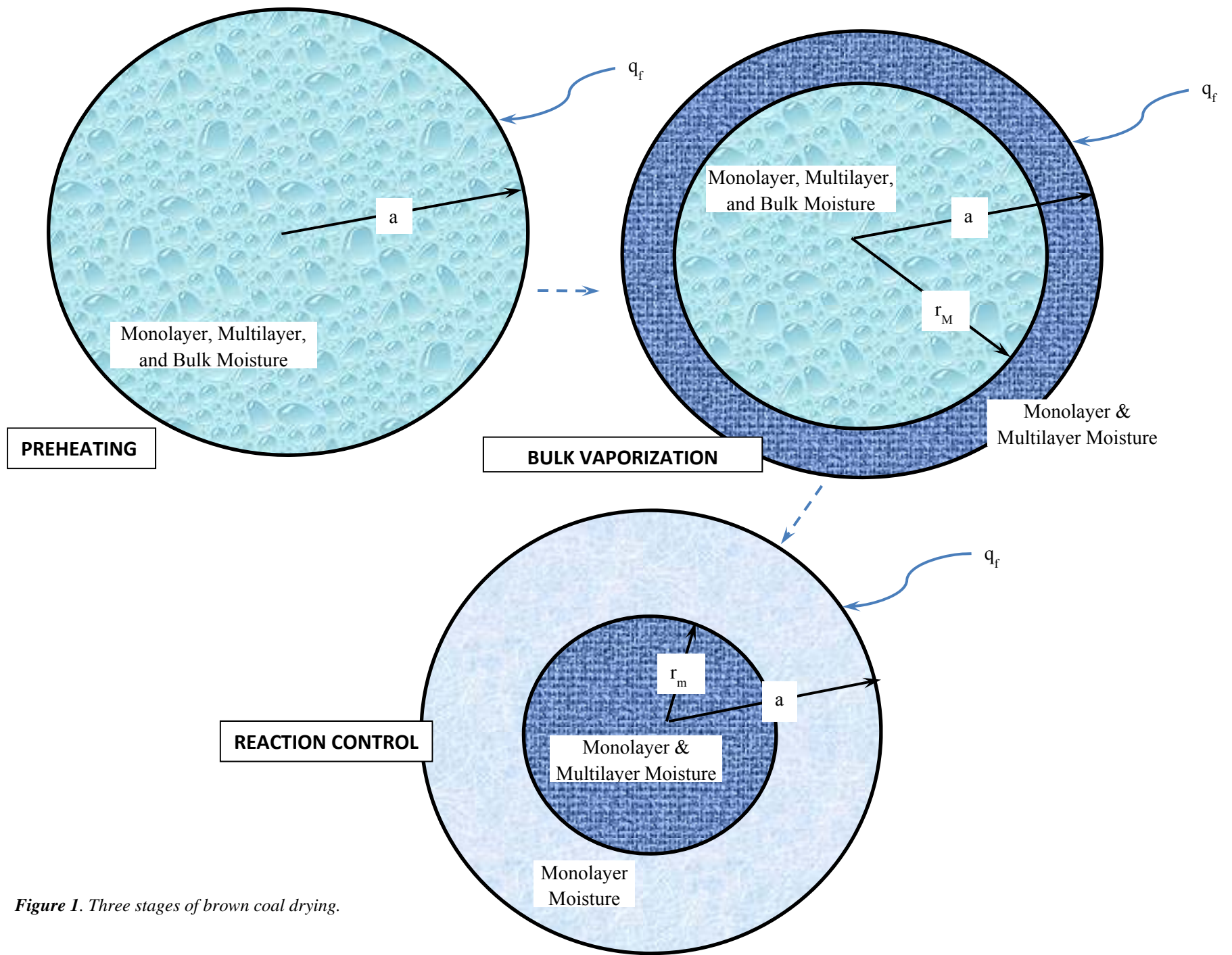
Figure 1. Three stages of brown coal drying.

associated with a physical adsorption/desorption processes with weak chemical interactions. The two pseudo-frequency factors are the only adjustable parameters in the analysis. Both values were set to interpret the datasets in this paper, and are the same for all brown coal samples. The reaction rate for moisture loss is first order with respect to the component moisture fraction. The surface coverages of multi- and monolayer moisture in equilibrium with the mole fraction of steam in the free stream, at the free stream temperature and pressure, are represented by BET adsorption isotherms whose parameters are based on the values reported by Allardice and Evans [2] in terms of linear regressions in temperature. The enthalpies of vaporization were enhanced by 5 and 25 % for multi- and monolayer moisture, respectively. Predicted drying histories are insensitive to the magnitudes of these enhancements.

The distinctive drying behavior of individual brown coal samples is cast in terms of the initial mass fractions of the three types of moisture. NEA's moisture estimation scheme is based on the equilibrium moisture content (EMC) as a function of relative humidity (RH) at 30°C, which has already been reported for numerous coal samples [3-5]. Monolayer moisture was assigned as the EMC at RH of 22 %. Bulk moisture was assigned from the EMC at RH of 93 % and from the bed moisture, which was based on the EMC at RH of 98 %. Once the bulk and monolayer moisture fractions are calculated, the multilayer moisture is assigned by difference with the total moisture level. Ultimately, the levels of the three types of moisture have been correlated with variables from the proximate and ultimate analysis, which are the only sample-specific input requirement. When applied to an assortment of Australian brown coals, this estimation procedure gave broad variations in the levels of the three types of moisture among individual samples. Bulk moisture constitutes 57 to 80 % of the total moisture; multilayer moisture constitutes 19 to 34 %; and monolayer moisture constitutes 1 to 11 %. These variations in the level of each form of moisture are definitely large enough to significantly affect the drying times and enthalpy requirements under some, but not all, drying conditions.

Each simulation of a complete drying history takes 5 to 10 min on an ordinary desktop PC, although some cases took as long as 25 min.

Validation With Reported Drying Histories
This section presents validations of the model results with data from three laboratory studies that characterized steam drying to moderate temperatures for a wide range of pressures. In the study of Bongers et al. [6], pressurized steam drying of low ash Loy Yang (LYLA) coal was examined in a batch autoclave from 180 to 230°C at 1 MPa. The test coal had 62 % moisture with 41 % bulk moisture; 16 % multilayer; and 5 % monolayer moisture. At 1 MPa, the dried coals reached their EMCs after 20 h of drying at all temperatures. For LYLA, increasing the residence time to 112 h did not change the EMC. Conversely, increasing the drying temperature above 185°C at 1 MPa to impose five degrees of superheat was sufficient to attain the EMC. Since the particle size of the coal was not provided, this value was estimated by a calibration simulation at 182°C and 1 MPa and uniformly applied to the remainder of the test conditions.

The evaluation of the residual moisture fractions after a residence time of 20 h is presented in Fig. 2. After a residence time of 20 h, the measured moisture content of the coal decreased from 62 % to 5 % at 222°C whereas the calculated values dropped from 62 % to 1 % moisture. While the general profile of the predicted residual coal mass and the moisture content as a function of temperature is consistent with the measured values, the relatively steep drop in the moisture level at183°C is depicted as a more gradual removal of moisture.

The steam drying experiments of Favas et al. [7] were conducted between 130 and 350°C for 30 min after the autoclave reached the test temperature. The size of the coal particles was estimated by calibration runs at 150°C at the corresponding steam saturation pressure for different particle sizes. For 5 mm, the calculated preheating time was approximately 15 min, similar to the value reported by Favas et al.
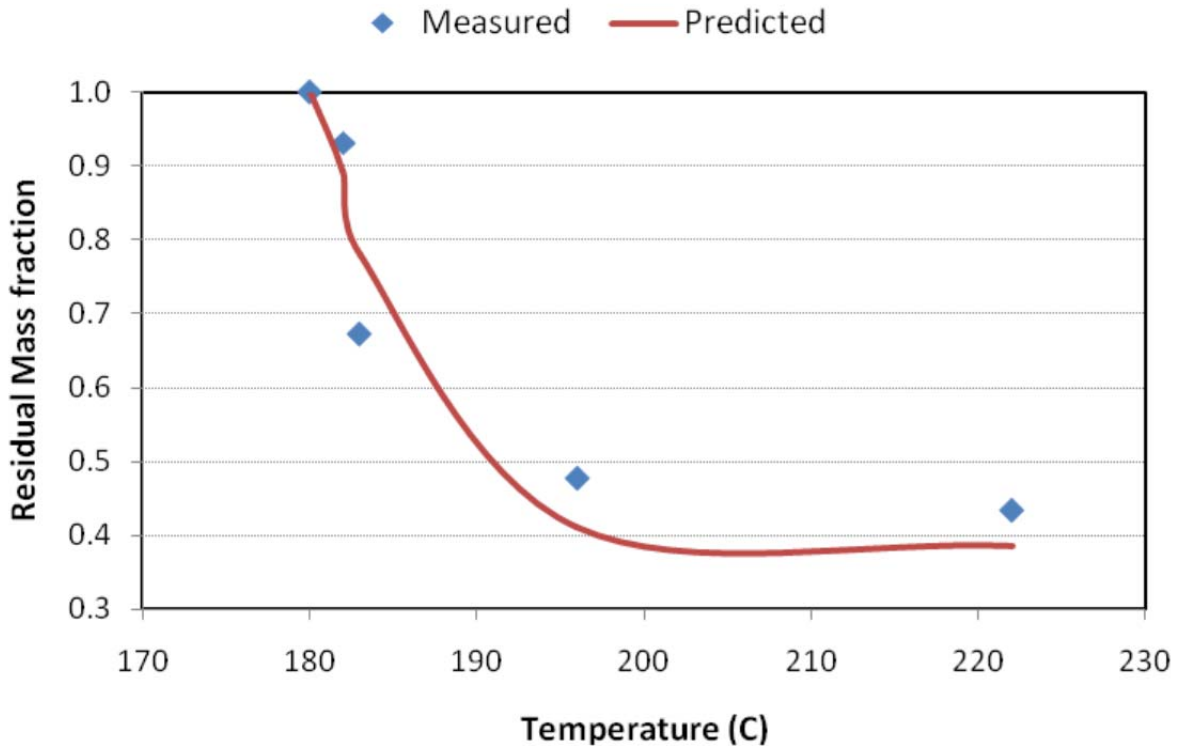
Figure 2. *Residual mass fraction of LYLA coal for different degrees of superheat for the tests of Bongers et al. [6].*

This size was used in all other simulations. The coal contained 60 % moisture with 37 % bulk, 18 % multilayer and 5 % monolayer moisture. Unfortunately, the test pressure was not reported. To calibrate it, the steam pressure in simulations was adjusted continuously until the calculated moisture content of the coal after 30 min matched the measured values at 130 and 230°C. At 130°C, the estimated degree of superheat was 2.15°C whereas at 230°C, it was 17 degrees. For the rest of the temperatures, a linear interpolation was used to first calculate the degrees of superheat and then to estimate the corresponding pressure.

The predicted residual moisture fractions evaluated in Fig. 3. In these comparisons, the residual coal mass is corrected to represent only moisture loss since, at 250°C, the coal recovery was only 95.5 %, with the remainder being coal decomposition products. Throughout the temperature range, the measured and predicted values are in excellent agreement indicating an adequate representation of the degrees of superheat. For these tests, the residence time was relatively short so only bulk moisture was removed, and the rates of multi- and monolayer moisture loss did not come into play except for a marginal contribution from multilayer moisture at 250°C.

Beeby et al. [8] monitored steam drying at atmospheric pressure from 101 to 178°C over extended holding times sufficient to achieve the EMCs. The coal properties were not reported so we used the properties of Yallourn coal (YL) in other tests reported by the authors [9]; the total moisture was 64 %, and the bulk, multilayer and monolayer moisture fractions were 42, 14, and 8 %, respectively. While the particles sizes were not directly reported, the associated cost analysis was performed using a 1 mm size particle, which we used in our calculations.

The calculated drying curve for the YL coal at 140°C is presented in Fig. 4. The residual mass fraction of
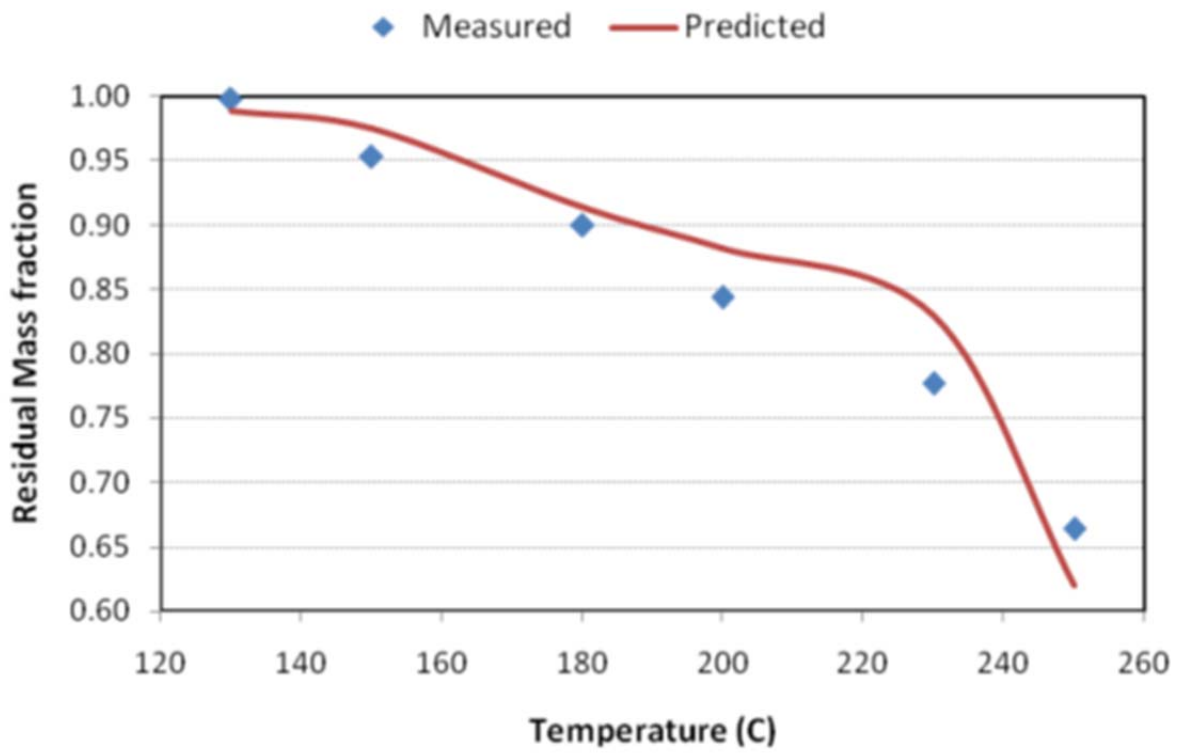
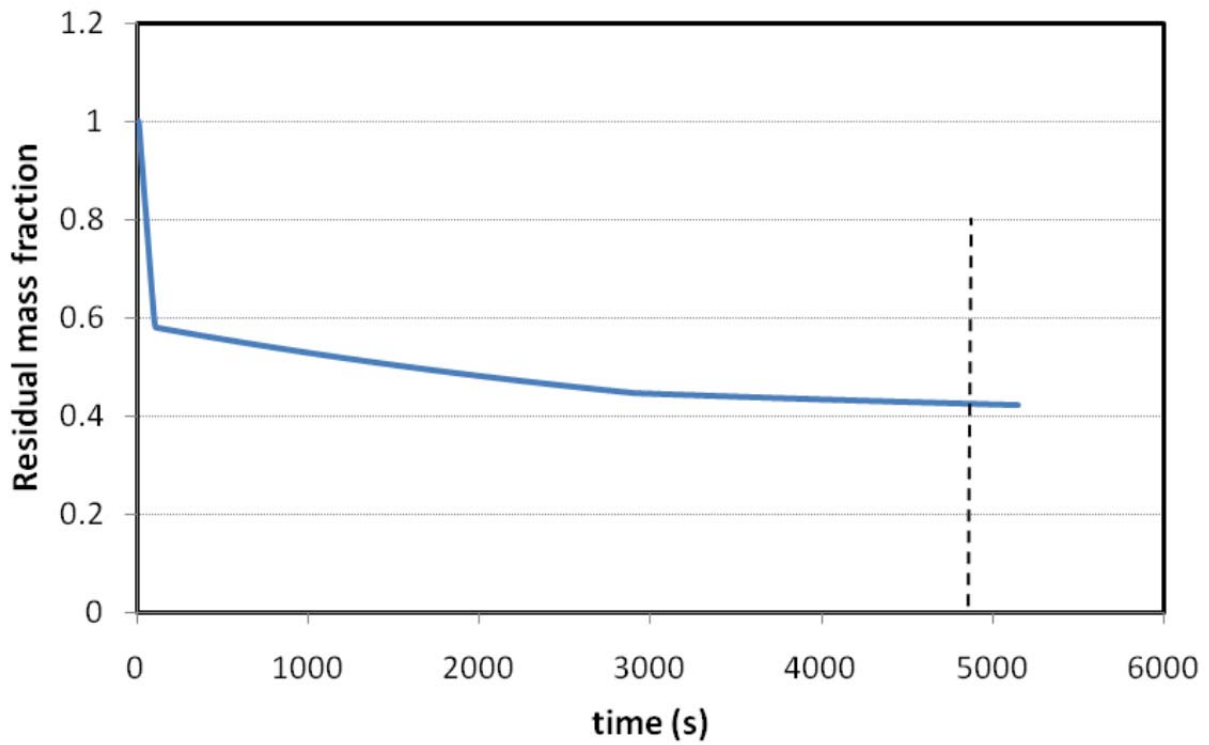*Figure 3*. *Residual moisture fractions at different temperatures for the tests of Favas et al. (2003) [7].*
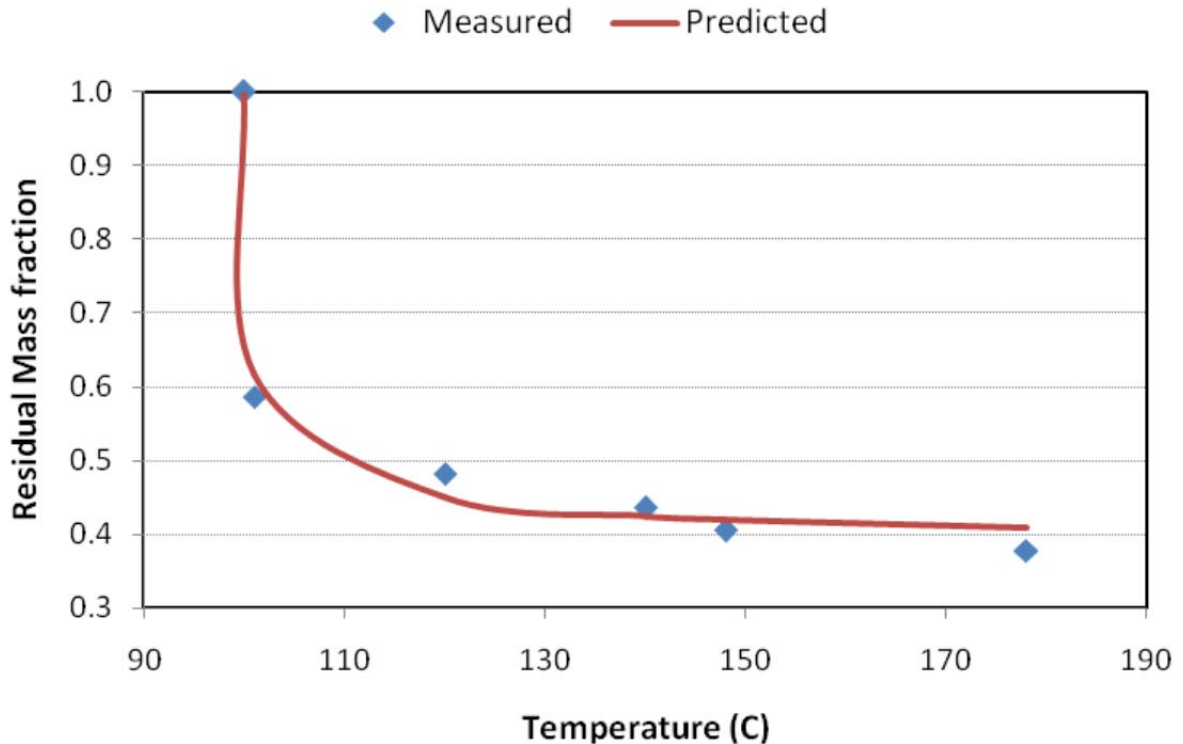

Figure 4. *Predicted drying curve at 140°C for the tests of Beeby et al. [8].*

Figure 5. *Residual moisture fractions at different temperatures for the tests of Beeby et al. [8].*

the coal was approximately 0.44, which corresponds to the EMC of 17 % that was measured at 4900 s. This time was applied as the residence time for all simulations at the different temperatures. As apparent from the three different segments of the drying curve, bulk moisture is removed much faster than both other forms, as expected. At the end of the bulk vaporization period of 120 s, the residual moisture is 38 wt. %. Subsequent removals of multi- and monolayer moisture are very slow. About 3000 s is required to completely remove multilayer moisture, at which point, the coal moisture content is about 20 %. Further removal of monolayer moisture is very slow, such that an additional 1900 s decreases the moisture only from 20 to 17 %. Our simulations suggest that a residence time of approximately 8200 s is required to reduce the coal moisture to 10 wt. % and 23,000 s are needed for complete moisture removal.

Once the residence time was estimated at 140°C according to the procedure stated above, the predictions were in excellent agreement with the measured values throughout the temperature range of operation, as seen in Fig. 5. At a low superheat condition at 101°C, only bulk moisture was removed, whereas multi- and monolayer moistures were removed at the higher temperatures. The most distinctive feature of the predictions is that at 101°C after approximately 1600 s, the bulk moisture vaporization ceased and there was no further progression of the bulk vaporization front towards the particle center. Evidently, the degree of superheat and the temperature gradients within the particle were too weak to drive the front forward to remove additional moisture.

Impact of Variations In Moisture On Drying Times
This section illustrates how variations in the three forms of moisture affect drying times. Four samples that nearly cover the domain of moisture variations for Australian brown coals were compiled from the reported properties of Yallourn (YL), low ash Loy Yang (LYLA), Morewell No.1 (MOR1), and Bowmans (BOW) coals. Based on our correlations with coal composition, the total bed moisture in these coals varies between 52 and 64 wt. %. Monolayer moisture varies between 2.3 and 7.2 wt. %; multilayer moisture varies between 8.9 and 20.3 wt %; and bulk moisture varies between 36 and 43.2 wt %. The

Table 1. *Times for preheating, and to remove bulk, multi-, and monolayer moisture, and the drying efficiency.*

Coal Label	$^{PRE}t_{MAX}$ (s)	$^{b}t_{MAX}$ (s)	$^{M}t_{MAX}$ (s)	$t_{M10\%}$ (s)	η_{DRY} (%)
YL	42	415	6200	10500	95
LYLA	41	383	9577	8147	93
MOR1	38	323	6856	9555	94
BOW	36	381	5715	5620	91

LYLA coal has the lowest monolayer and the highest multilayer moisture; the YL coal has the highest bulk and monolayer moisture; MOR1 has the lowest bulk moisture; and BOW has the lowest multilayer moisture.

Coal particles of 2 mm diameter were steam dried in a fluidized bed at a slightly subatmospheric pressure of 0.95 atm and 145°C. The feed steam contained 5 % nitrogen. The simulations were then run to complete dryness. The drying times corresponding to the different stages of drying are reported in Table 1 for the four coals. The table reports the preheating time ($^{PRE}t_{MAX}$), the end of bulk moisture vaporization ($^{b}t_{MAX}$), the end of multilayer moisture vaporization ($^{M}t_{MAX}$), and the time at which the total moisture content of the coal is 10 wt. % ($t_{M10\%}$). These times are cumulative and do not express drying times for individual stages. The corresponding drying efficiency, η_{DRY}, appears in the final column.

It is clear from the predictions that the drying time is not solely a function of the total moisture content of the coal. Time $t_{M10\%}$ was longest and shortest for the YL and BOW coals, respectively, which had the highest and lowest total moisture. But the times for LYLA and MOR1 did not correlate with their total moisture contents. For all coals, the preheating periods were relatively very short. Similarly, the variation in bulk moisture from 36 to 43.2 % changed the bulk vaporization period by less than 100 s, which is insignificant compared to $t_{M10\%}$. Consequently, variations in the bulk moisture levels in the range examined for Australian coals do not have any significant impact on the drying time. Since the bulk moisture vaporization times are similar, the time for multilayer moisture removal is determined by the level of multilayer moisture, as expected. Comparing $^{M}t_{MAX}$ and $t_{M10\%}$ shows that coals with more multilayer moisture dry faster than those with more monolayer moisture. The 10 wt. % moisture targets for LYLA and BOW were reached during multilayer moisture vaporization; consequently, they dried faster than YL and MOR1 coals because multilayer moisture is released faster than monolayer moisture. For a 2 mm particle dried in steam under slightly subatmospheric conditions, the drying time to achieve a target moisture level increases with the total moisture in the coal and the level of monolayer moisture, provided that the ultimate target moisture level requires the release of appreciable monolayer moisture.

Summary

Our current validation database represents temperatures from 100 to 250°C, pressures from 0.1 to more than 1 MPa, and drying times to several thousand seconds. Throughout this entire domain of drying conditions, the simulation results accurately describe both the residual moisture fraction and the moisture content as functions of the steam drying conditions. This performance is especially noteworthy because none of the drying rate parameters were adjusted to improve the agreement with data in any of the test cases. All the simulation results for all the data comparisons are based on the same drying parameters.
For drying temperatures near the normal boiling point of water, bulk moisture vaporization stops even before the bulk vaporization front reaches the particle center, so that only part of the bulk moisture is removed. The drying curve and the moisture concentration profiles remain steady because the temperature gradients within the particle are too weak to remove additional bulk moisture. But for the

hotter temperatures and greater degrees of superheat in many commercial drying processes, both the preheating stage and the bulk vaporization stages make negligible contributions to the total drying times. Since most of the moisture in all brown coals is bulk moisture, its rapid elimination obscures the relationship between total moisture and the time needed to achieve a target moisture level. But the drying curves of residual moisture vs. time from this analysis clearly depict the sudden deceleration in the drying rate when bulk moisture is eliminated and multilayer moisture begins to vaporize, and a second, more moderate deceleration, when multilayer moisture is eliminated and monolayer moisture begins to vaporize. Indeed, it is these two transitions, rather than the total moisture level, that determine drying times to a target moisture level.

Sensitivity studies for coals with different levels of the three moisture types clearly demonstrate that the drying time is not solely a function of the total moisture content of the coal. For some selections of coal samples, drying time will be proportional to total moisture, and for other selections, there will be exceptions. One such exception was demonstrated in our sensitivity studies. For typical concentrations of the three forms of moisture in brown coals, one key aspect is whether or not the target moisture level requires removal of any monolayer moisture at all. Coals with abundant bulk and multilayer moisture can achieve targets of, say, 10 % residual moisture by vaporizing only a portion of the multilayer moisture. Consequently, their drying times and enthalpy requirements will be relatively modest. But coals with little bulk moisture and relatively abundant monolayer moisture will require relatively long drying times simply because monolayer moisture is always released much more slowly than multilayer moisture. Hence, the distribution of the three forms of moisture in any particular coal sample is an important determining factor for both drying time and enthalpy requirements.

Acknowledgement

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