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The Analytical Theory of Water Activity in the Paddy Rice Drying Process

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Abstract: Drying involves the evaporation of moisture, accompanied by simultaneous heat transfer, mass transfer, and momentum transfer. While the diffusion law is considered an applicable model for explaining the drying phenomenon, the actual drying process cannot be accurately predicted using an analytical solution with a constant diffusion coefficient. Energy efficiency in the drying process is low due to an insufficient understanding of the mechanisms governing moisture migration from solids to air. The development of drying theory has stalled due to an unsolvable discrepancy between experimental results and analytical results. This study analyzes the effect of the binding energy of moisture in paddy rice on the diffusion coefficient. The theoretical relationship between water activity and drying rate in paddy rice was investigated, and the drying process was successfully explained by analyzing free energy transfer and transition theory. The mechanism of rice grain drying was described using a new theoretical solution for the drying process. These results provide new insights into the development of a scientific evaluation standard for assessing the efficiency of actual drying processes.

Keywords: paddy rice; free energy; drying technology; theoretical solution

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1. Introduction

The transfer laws of heat, mass, and momentum regulate the drying phenomenon. However, each of these transfer laws describes a specific behavior within the phenomenon. When applied, these conditions must satisfy not only their respective singularity criteria but also geometric, physical, temporal, and boundary conditions. The simultaneous transfer of heat, mass, and momentum during the drying process makes it challenging to derive a mathematically precise solution for the transfer coefficients [1]. The diffusion models yield significant errors when the diffusion coefficient is treated as a constant, resulting in discrepancies compared to actual conditions. Furthermore, drying mechanism models based on diffusion kinetics face challenges in accurately quantifying the activation energy, pre-exponential factor, and process exponent [2,3].

Researchers have modeled moisture migration as continuous medium flow, using time and space continuous functions and applying Fick's law and the Fourier heat conduction equation. They have employed the Eulerian method, Lagrangian method, and volume averaging method [4,5], establishing numerous drying models tailored to specific material systems [6–9]. Researchers have differentiated mass transfer within materials into capillary flow and vapor diffusion motion in accordance with the laws of mass and energy conservation and the principles of irreversible thermodynamics. Various drying differential equation sets have been established based on temperature, concentration, and pressure potential fields [9–13]. Using computer simulation, researchers developed pore network models to analyze the drying process and investigated calculation parameters for a series of models [14,15]. Researchers have observed that materials undergo a slowed drying

process under conditions where the evaporation surface recedes inward from the outer surface and the area gradually decreases [16–18]. Materials are simplified by considering the vaporization interface as the boundary, with a wet zone inside the interface and a dry zone outside, assumed to be in complete equilibrium. Various diffusion models have been developed to analyze specific material drying processes. As the drying progresses, real-time changes in the material's physical properties lead to complex physicochemical and biochemical reactions, volume shrinkage, texture, and configuration alterations, which in turn affect pore structure, tortuosity, and moisture transport pathways, influencing overall intensity. This results in discrepancies between the actual process and the idealized diffusion at the interface [19–23]. The drying process does not conform strictly to coefficient diffusion, revealing deficiencies in existing drying models and incomplete theoretical descriptions [24].

During actual drying processes, moisture and temperature vary between the inside and outside of rice grains. The state changes in moisture vaporization and migration processes within rice grains demonstrate significant inertia and nonlinear characteristics, differing from ideal gas behavior [25,26]. This fundamental difference distinguishes rice drying from the quantitative material systems and ideal processes described in general thermodynamics [27,28].

Moisture vaporization and migration are spontaneous processes, making water activity an intrinsic property of rice. Experimental data under steady-state conditions allow for an accurate correlation between water activity and external condition parameters. Moisture migration is influenced by free energy [28,29], which represents the energy available in a material system to perform technical work in the external environment. This phenomenon can be observed through molecular or microscopic motion or described through heat and mass transfer phenomena during the process [29–32]. Following this research approach, researchers have derived the theoretical expression for grain moisture binding energy [27] and provided mathematical solutions for the vaporization latent heat coefficient and drying characteristic function of grain moisture. By establishing the theoretical link between rice water activity and drying rate and integrating the transfer and conversion of free energy as a unified metric [28,33], this study explores the binding energy of rice moisture. It presents a theoretical framework for understanding the rice drying process and outlines practical applications.

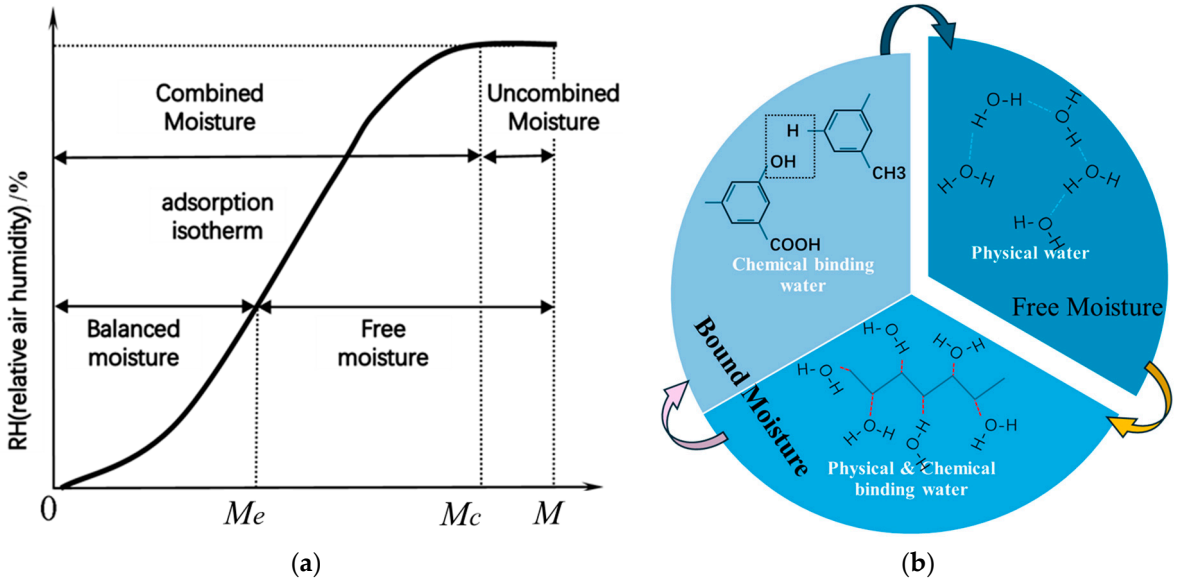
This study aims to establish a rigorous mathematical relationship between the drying rate of rice grains and the consumption of free energy during moisture evaporation while also revealing the theoretical solution for the water-binding energy of rice grains. Therefore, the theoretical heat consumption of rice grain drying can be evaluated under various environmental conditions. In practical applications, this study not only analyzes the drying process of rice grains at specific phases but also establishes a theoretical framework for predicting the drying process under a variety of external conditions through these analyses. These findings provide a theoretical basis for objectively evaluating the drying efficiency of rice grains in any actual drying process and for developing scientific standards to evaluate energy utilization efficiency in drying equipment systems.

2. The Paddy Rice Drying Theory

2.1. The Moisture Content in Paddy Rice

In the field of drying technology, moisture-binding in materials is categorized into chemically bound water, physicochemically bound water, and physical–mechanically bound water. Chemically bound water showed strict quantitative relationships, whereas physicochemical-bound water, which lacks such strict quantification, can be further categorized into (1) adsorption-bound water, a liquid confined by force fields on external and internal surfaces of "capsules", and (2) osmotically maintained water, encompassing expansion water and structural water, sealed within cells. This category includes water adsorbed by composite capsules through osmotic absorption and fixed structural water. Free water, due to its low binding energy, is classified separately from physical–mechanically bound

water, which can vary in quantity and is present in both large and small capillaries within materials. In drying engineering, regardless of the form in which moisture exists in the material, the primary focus is on the amount of moisture that can be removed from the wet material and the associated energy consumption. Based on equilibrium characteristics, moisture can be categorized as bound moisture or free moisture, depending on the relative humidity of the air and the moisture content of the material, as illustrated in Figure 1a,b.



(**a**) (**b**)

Figure 1. (**a**) The moisture content changed with RH. (**b**) The forms of moisture in Paddy Rice.

The activity of non-bound water is equal to 1, and its evaporation was unaffected by the material, similar to the evaporation of a free liquid surface. The rate of vaporization remained solely dependent on external conditions. Bound moisture refers to the moisture contained within rice grains, where, under steady-state conditions, evaporation characteristics are primarily governed by the physical properties of the rice. The evaporation rate corresponds to the prevailing environmental conditions and is influenced by water activity [34].

2.2. Two-Staged Characteristics of Paddy Drying

Paddy rice comprises two parts: the husk and the grain, which differ significantly in texture. The husk, with its loose texture, surrounds the grain and facilitates easier drying. Therefore, the drying process of rice is characterized by a two-stage decrease in drying rate [35]. During the initial stage of drying, moisture distribution inside and outside the rice was uniform and consistent, with moisture exhibiting zero binding energy. At this stage, the drying rate was at its maximum, while with the progress of the drying process, the husk first encountered the external medium, gradually disrupting the thermal equilibrium between the husk and the grain. This phenomenon led to a significant decrease in the drying rate during the initial stage (Stage I) of drying. As drying progresses and the moisture content of the husk decreases rapidly, the drying rate subsequently slows down, primarily influenced by internal moisture diffusion within the grains, leading to a two-stage decrease in drying rate, as illustrated in Figure 2.

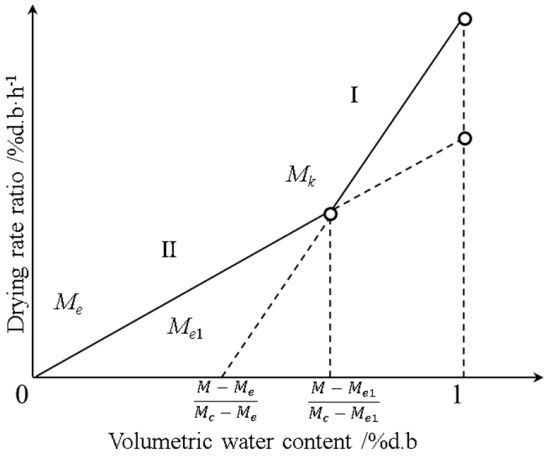


Figure 2. Two−stage characteristics of paddy drying Note: I and II denote the 1st and 2nd descending drying sections, respectively. M_e represents the equilibrium moisture content (% d.b.), M_{e1} represents the equilibrium moisture content (% d.b.) of the 1st descending drying section, M_k is the cut−off moisture content (%), and M_c is the initial moisture content (% d.b.).

3. Theory Analytic Methods

3.1. The Free Energy Consumption in the Moisture Evaporation

The drying process can be quantitatively explained by considering both the amount of moisture migration and its migration potential, determined by the material system's state parameters [36]. Furthermore, all processes dependent on thermodynamic state parameters can be attributed to enthalpy. Understanding the energy input into the drying system allows us to describe changes in both the system and its materials using state functions, regardless of the form of water present or alterations in the drying mechanism parameter. Therefore, the enthalpy of any given drying state point may be used to determine the thermal energy consumption at that state point, regardless of the conditions. This calculation facilitates the derivation of the expression for the material's internal moisture binding energy, represented as Equation (1) [27].

$$\mu = -\int_{p_s}^{p} v dp = -R_{pn} T \ln \varphi \quad (1)$$

where ϕ is the water activity, $\phi = \frac{p}{p_s}$, P represents the vapor fraction pressure, Pa; T is the vaporization temperature of water, K; p_s is the saturated vapor pressure, Pa; R_{pn} is the interval characteristic constant $R_{pn} = \frac{\int_{p_s}^{p} c_p d(\ln p)}{p - p_s}$; c_p is the specific heat of water vapor at constant pressure, kJ/kg, with a fixed value at each state point. In [p_s, p] interval, isothermal test condition, $R_{pn} = \frac{\sum_{i=1}^{n} c_{pi}}{n}$, kJ/kg·K^{-1}; c_{pi} is the specific heat value, kJ/kg, corresponding to different pressures under isothermal conditions.

Similarly, it is feasible to experimentally ascertain the specific heat at constant pressure at varying temperatures under equilibrium pressure conditions. The physical significance of R_{pn} was almost similar to the average specific heat at constant pressure throughout the state changes occurring during the process of moisture vaporization.

The free energy expended during moisture vaporization reflects the ability of water vapor to perform external work. Letting f denote the specific free energy consumption of water vaporization in its free state (measured in kJ/kg), the rate of change in the system's free energy is given by $df = pdv$.

Because the specific volume of water vapor is much larger than that of liquid water at the same temperature, the specific volume of water can be considered negligible in comparison. Thus, when the water activity equals 1, the integral expression for the free

energy consumption required to vaporize 1 kg of moisture in the material system can be expressed as Equation (2).

$$\int_0^f df = \int_0^v pdv \tag{2}$$

Due to $dv = -\frac{c_p}{p^2}Tdp$, At the same temperature, p corresponds to v one by one. Thus, expression (2) can be rewritten as: $\int_0^f df = \int_0^p -\frac{c_p}{p}Tdp$. The specific free energy for vaporizing 1 kg of moisture was obtained through an integral calculation, which can be written as.

$$f = R_{pn}T \tag{3}$$

The free energy required per 1 kg of vaporized water is the sum of the terms presented in Formulas (1) and (3) upon moisture vaporization from the material. The expression for the free energy consumed per 1 kg of water vaporized from the material is represented as Equation (4), using the symbol f_g.

$$f_g = R_{pn}T + \mu = R_{pn}T(1 - \ln\phi) \tag{4}$$

Equation (4) indicates that the free energy consumed during moisture evaporation is a state function dependent on absolute temperature and water activity. Equation (4) applies to any material and vaporization process, holding universal significance. All specific properties associated with the internal structure and processes of the substance can be confirmed as real interval characteristic parameters R_{pn}. Concerning the microstructure and process variables of the material, no assumptions were made [36]. Using internationally recognized steam tables and experimental data within the temperature range of $0 \leq$ T $-273.15 \leq 100$ °C at one-atmosphere pressure, the constant characteristic formula for the state change interval of water vapor in [273.15, T] is derived as Equation (5).

$$\begin{gathered} R_{pn} = 2 \times 10^{-9}t^4 - 4 \times 10^{-7}t^3 + 4 \times 10^{-5}t^2 - 0.0015t + 2.3754 \\ t = T - 273.15 \end{gathered} \tag{5}$$

Expression (6) was derived by dividing Equation (4) by Equation (3), where the $1 - \ln\phi$ term denoted by the symbol Cz represents the specific free energy consumption coefficient.

$$C_z = \frac{f_g}{f} = 1 - \ln\phi \tag{6}$$

Expression (6) demonstrates that water activity equals 1 in a free state, with the specific free energy consumption coefficient also equaling 1. In the presence of water-binding energy, water activity was less than 1, resulting in a free energy ratio greater than 1. When vaporized from the material, the same amount of water consumed $1 - \ln\phi$ times heat compared to its free state.

3.2. The Free Energy Balance Equation for the Evaporation Process

Regardless of the circumstances, the vaporization of an equivalent amount of moisture from any material consistently required the same quantity of free energy. Assuming the material's moisture content is M_0 (% d.b.) at a water activity level of 1, the equilibrium moisture content is represented by Me (% d.b.). The maximum drying rate (% d.b.h^{-1}) and drying rate (% d.b.h^{-1}) within the drying interval M ($M_e \leq M \leq M_0$) can be represented by symbols $\left(-\frac{dM}{d\theta}\right)_{\max}$ and $-\frac{dM}{d\theta}$, respectively. The reduction $-\frac{dM}{d\theta}$ relative to the $\left(-\frac{dM}{d\theta}\right)_{\max}$ was found to correspond to the additional free energy consumption required for the evaporation of water constrained within the material, leading to the derivation of equilibrium Equation (7) that describes the relationship between free energy consumption.

Simplifying Equation (4) provided the inherent drying rate ratio state function expression (8) of the material.

$$f\frac{dM}{d\theta} + \mu\frac{dM}{d\theta} = f\left(\frac{dM}{d\theta}\right)_{\max} \tag{7}$$

$$\frac{-\frac{dM}{d\theta}}{\left(-\frac{\mathrm{d}M}{\mathrm{d}\theta}\right)_{\max}} = \frac{f}{f+\mu} \tag{8}$$

where $f = R_{pn}T$ is the free energy of 1 kg water vapor with 1 equivalent of water activity, kJ/kg; θ denotes drying time, and M represents the dry base moisture content of the material, % d.b.

By substituting Formulas (1) and (3) into Formula (8), an expression (9) was obtained for the drying rate ratio state function.

$$\frac{-\frac{dM}{d\theta}}{\left(-\frac{\mathrm{d}M}{\mathrm{d}\theta}\right)_{\max}} = \frac{1}{1-\ln\varphi},\ 0 < \max \leq 1 \tag{9}$$

Equations (7)–(9), $-\frac{dM}{d\theta}$, and $\left(-\frac{dM}{d\theta}\right)_{\max}$ represent the theoretical drying rate and maximum drying rate inherent to the material itself, reflecting the drying rates that can theoretically be achieved by the material. The $\frac{1}{1-\ln\varphi}$ in Equation (9) represents the theoretical drying rate ratio of the material in an ideal, perfectly dry medium under steady-state conditions, often referred to as the theoretical drying rate ratio.

Equation (9) reveals that the theoretical drying rate ratio is a single-valued function of the moisture content of the material. Under isothermal conditions, φ is a single-valued function of M, a mass ratio expressed in % d.b., and remains unaffected by the moisture distribution within the material. Therefore, Equation (9) can be used to express the drying rate ratio for any drying process and the corresponding moisture content state.

3.3. Characteristics of Theoretical Drying Rate Ratio

The theoretical drying rate ratio is a single-valued function of water activity. Therefore, the theoretical drying rate ratio can be determined by Equation (9), as illustrated in Figure 3, under steady-state drying conditions as a function of water activity within the range of [1, 0).

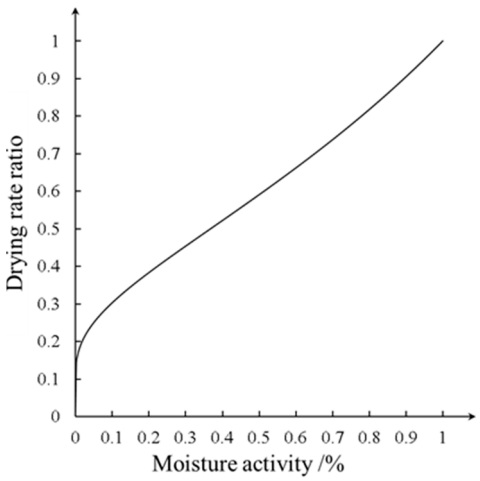


Figure 3. The changes in drying rate ratio with different water activities.

Water activity indicates the extent of moisture binding and resistance to moisture migration, which affects the consumption of free energy during the moisture migration process and is influenced by the dry matter components' resistance.

As depicted in Figure 4, higher water activity values correspond to greater drying rate ratios, indicating a lower degree of binding and smaller binding energy between the moisture and dry matter components. Conversely, lower water activity values correspond

to higher degrees of binding and larger binding energies between the moisture and dry matter components. As water activity approaches zero, the drying rate ratio similarly approaches zero. Throughout this process, even slight fluctuations in water activity can lead to notable variations in the drying rate ratio.

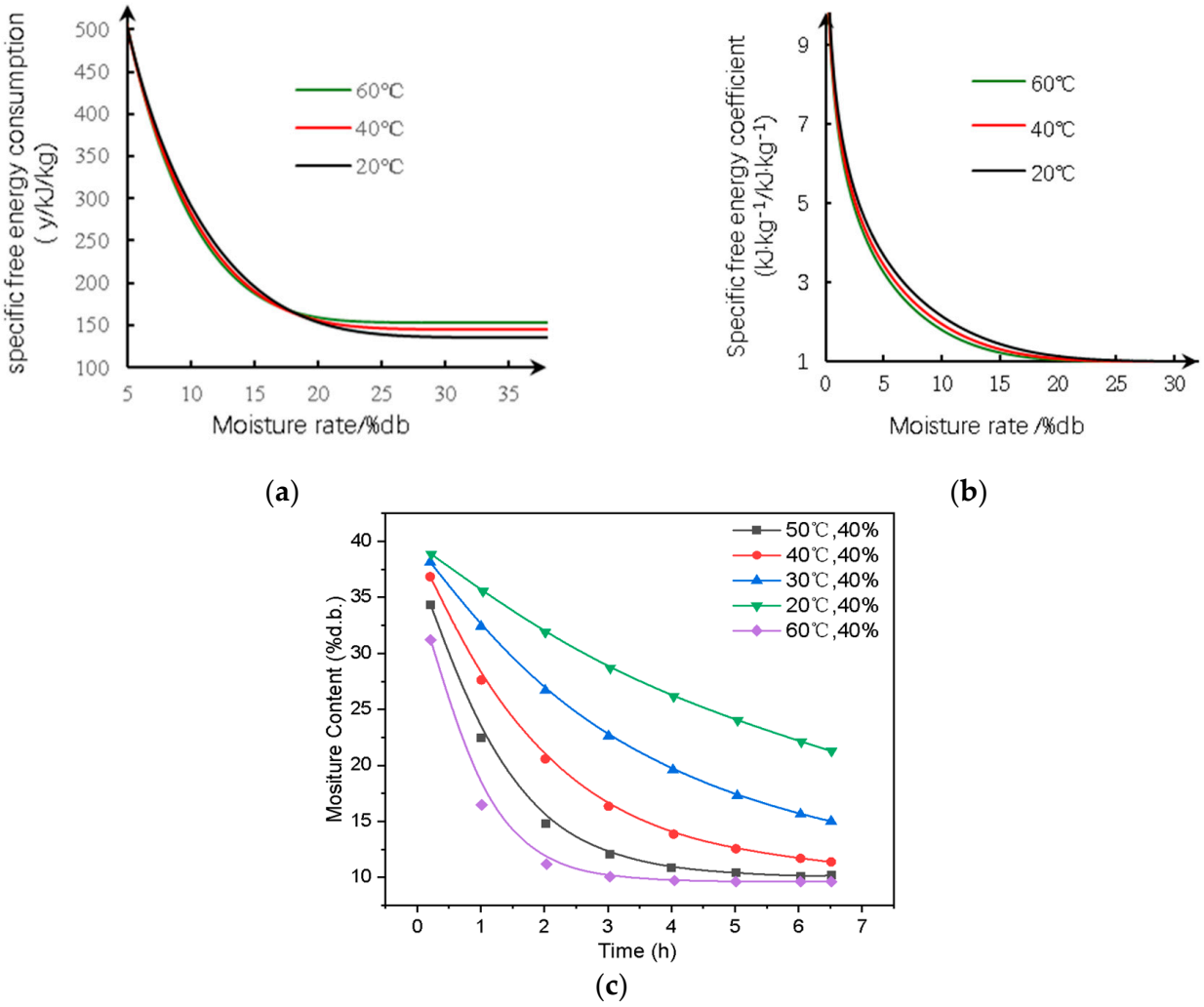


Figure 4. (**a**) The variation pattern of rice water activity. (**b**) The theoretical drying rate ratio of rice. (**c**) Change in moisture content in grain.

3.4. The Water Activity Model for Paddy Rice

Water activity is influenced by the moisture content and temperature of the material and serves as an inherent characteristic function of the material itself. Under steady-state conditions, the equilibrium moisture content represents the maximum moisture level that the material can attain during the drying process. It signifies the moisture content at which the material fully returns to its environmental state.

Various equations have been proposed by different research institutions and scholars across different countries to calculate the equilibrium moisture content for various types of materials. These equations are collectively referred to as equilibrium moisture content models [37–39].

Since equilibrium moisture content can be accurately determined under static experimental conditions, several precise formulas have been developed for various materials.

Equation (10) is among the widely recognized equilibrium moisture content models used internationally, particularly for grains [40].

$$M_e = \left[\frac{-\ln(1-\phi_{e)}}{A(T_a - 273.15 + B)}\right]^{\frac{1}{n}} \tag{10}$$

where T_a represents the temperature of water vaporization, K. M_e is the dry base equilibrium moisture content (%); A, B, and n represent the calculation parameters. For paddy, A = 1.9187×10^{-5}, B = 51.161, n = 2.4451 [28].

Equilibrium moisture content is a state function and can theoretically be expressed as $M_e = [f(T, \varphi)]_e$, where subscripts indicate constant temperature and humidity drying conditions. Based on Equation (10), the expression for the equilibrium relative humidity φ_e of the drying medium can be derived, as shown in Equation (11).

$$\phi_e = 1 - \exp[-M_e^n A(T_a - 273.15 + B)] \tag{11}$$

Under phase equilibrium conditions, the migration potential at each point within the material system was uniform, resulting in a zero mass migration gradient. The temperature and pressure inside and outside the material reach equilibrium, and all state parameters remain constant over time. Therefore, under phase equilibrium conditions, the water activity is numerically equal to the relative humidity of the medium, and it can be calculated based on the temperature and relative humidity of the medium. The drying phenomenon can be regarded as a transition from one equilibrium state to another when employing the general method of thermodynamic analysis. Therefore, Equation (12) can be used to represent the grain's water activity during the drying process.

$$\phi = 1 - \exp\left[-M^n A(T_g - 273.15 + B)\right] \tag{12}$$

where T_g is the material temperature, K; ϕ is the water activity; M represents the moisture content, % d.b.

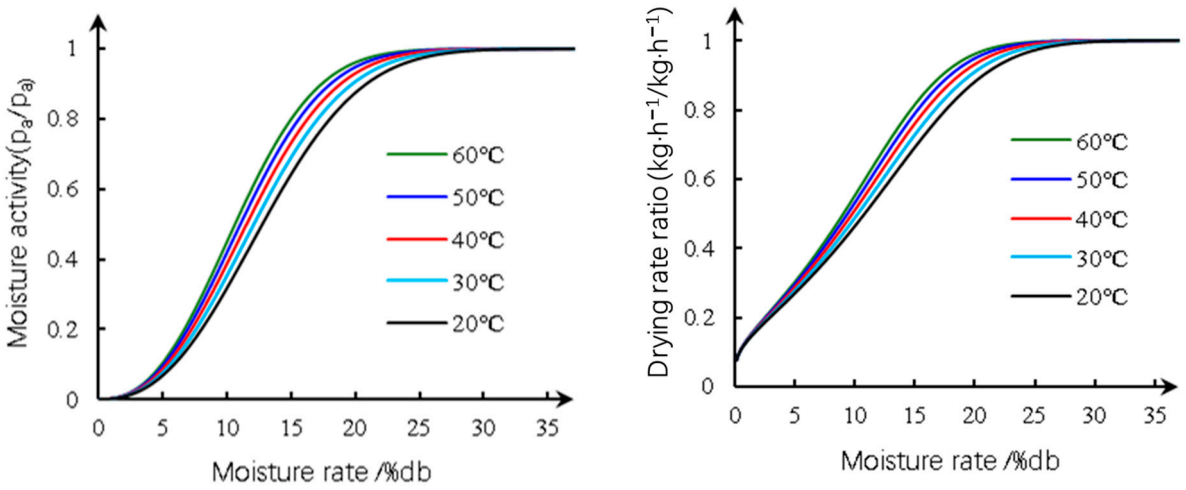
The moisture content and temperature of the material were the two independent variables in Equations (11) and (12). These two parameters are both state parameters of the drying material system; however, the physical meanings of Equations (11) and (12) are distinct. The water activity of the rice grain is an intrinsic property of the grain and acts as a state function dependent on the grain's temperature and moisture content. In contrast, the relative humidity of the surrounding medium is a state function determined by the temperature and moisture content of that medium.

4. Theoretical Analysis and Discussion

The free energy consumption ratio refers to the energy, expressed in kJ/kg, consumed by the material system to facilitate the movement of water vapor and exert external forces when 1 kg of water evaporates from the material. Energy consumption refers to the internal energy expended by the material system to perform this function.

Theoretically, it denotes the maximum technical work achievable after the evaporation of 1 kg of water from the material. During the drying process, the intrinsic energy of the rice grain is transformed into kinetic energy, which is necessary for the movement of water vapor [27].

Figure 4a illustrates the relationship between the free energy consumption ratio of rice grain during moisture evaporation and moisture content at various temperature conditions, as determined by Equations (4), (6), (9) and (12). Figure 4b illustrates the variation in the free energy coefficient with moisture content. Figure 5a illustrates the relationship between moisture content and water activity, while Figure 5b illustrates the theoretical drying rate ratio as determined from the analysis.



(**a**) (**b**)

Figure 5. (**a**) The consumption of free energy during the drying process of rice. (**b**) The variation pattern of the ratio of free energy during the drying process of rice.

Based on Figure 4a, it was evident that the free energy of rice grain decreased as the moisture content increased during slow drying. The impact of moisture content was more pronounced than that of temperature, especially at lower moisture levels. However, when the moisture content exceeded 25% d.b., changes in free energy were more closely associated with temperature, leading to an increase in values as temperature increased, approaching a constant state.

At this stage, the change in free energy related to moisture in the material can be described as a single-valued function of temperature, and the moisture evaporation process is equivalent to free surface evaporation. Therefore, it can be inferred that the drying process of the material with high moisture content can be simplified as constant-rate drying. The curves in Figure 4a intersect at varying temperatures, suggesting that the moisture evaporation rate in the rice hull was higher than that of the rice grain during the initial drying stage. As the temperature increased, the moisture content in the rice hull decreased, leading to a corresponding increase in the consumption of free energy by the rice hull.

The consumption ratio of free energy is a universal property that reflects all changes in drying material states. According to Equation (4), when the water activity was equal to 1, it demonstrated the 1 equivalent free energy consumption. However, if there was water binding energy and the water activity dropped below 1, the free energy consumption increased beyond 1.

In any drying process system, there exists a maximum drying rate state point, which corresponds to the highest water activity achievable under the same environmental conditions. As per Equation (4), the free energy required to convert moisture into vapor depends on the temperature and water activity. The change in free energy consumption during the drying process is solely determined by the water activity, assuming the temperature remains constant. Therefore, the free energy coefficient can be determined at any drying temperature by using Equation (12), which establishes a correlation between moisture content, temperature, and water activity. Figure 4b shows the variation in the free energy coefficient of rice grain during moisture evaporation under different temperature conditions. It is evident from Figure 4b that the free energy coefficient of rice grain during moisture evaporation increased as the moisture content decreased, regardless of the temperature. Furthermore, the free energy coefficient decreases with increasing temperature at a given moisture content. This indicated that as the temperature rose, the drying driving force increased, thereby reducing the free energy consumption during moisture evaporation.

In this study, we examined the moisture content variations over time in fresh rice grains, initially set at 40% moisture, by utilizing a thin-layer dryer within various drying

environments. The experimental setup included monitoring moisture levels, specifically in the central area of the drying chamber. As depicted in Figure 4c, our findings reveal that elevated temperatures significantly enhance the initial reduction in moisture content within the rice grains. However, during the later stages of the drying process, a marked deceleration in the rate of moisture loss was observed. This phenomenon can be attributed to the increased consumption of free energy when the rice grains reach lower moisture levels. The experimental outcomes align well with the predictions of our theoretical model, thereby validating the model's accuracy in simulating the drying process of rice grains.

Water activity is also dimensionless, with a range of (0, 1). It is evident from Figure 5a that the moisture content change varied most significantly at 0 and progressively decreased toward the maximum value at the same water activity under different temperature conditions. Similarly, the change in water activity difference under varying temperature conditions at the same moisture content followed a pattern of initiating at 0, reaching a maximum, and then declining toward 0. When the moisture content of rice grain exceeded 30% d.b., the water activity of the material closely approached that of a free state. However, when the moisture content was below 5%, the water activity was very low and gradually decreased with decreasing moisture content. This indicated that the binding force of moisture to the dry matter components of rice grain rapidly increased with decreasing moisture content, following a nonlinear process.

In two geometrically similar drying systems, if they share the same material water activity or the difference between material water activity and the relative humidity of the medium, their drying rates relative to the maximum drying rate under those conditions should be identical. A lower drying rate ratio indicates greater binding energy between the material and moisture, reflecting an inherent property of the material itself. Therefore, the drying rate ratio expresses the intrinsic drying mechanism of the material itself, independent of dimensions, and comprehensively describes the principles of material drying, revealing its fundamental nature. Therefore, regardless of the distribution of water within the material or changes in other parameters of the drying mechanism, the drying phenomenon can be quantified using the state function of the drying rate ratio. Figure 5b illustrates the variation in the rice grain drying rate ratio with moisture content under different temperature conditions. It is apparent that at the same theoretical drying rate ratio level, the difference in moisture content change under various temperature conditions followed a pattern of starting at 0, reaching a peak, and then decreasing back towards 0.

Similarly, at identical moisture content, the variation in water activity difference under different temperature conditions followed a pattern of starting at 0, reaching a peak, and then decreasing towards 0. When the moisture content of rice grain surpassed 30% d.b., the theoretical drying rate ratio showed minimal variation. As the drying progressed into the falling rate stage with water activity below 1, the theoretical drying rate ratio decreased rapidly with decreasing moisture content. Moreover, at the same moisture content, the higher temperature led to a higher drying rate ratio. However, the influence of temperature on the drying rate ratio was less significant when the moisture content was reduced to about 5% d.b. The differences in both vertical and horizontal dimensions between the curves in Figure 5b distinctly illustrate that the drying process of rice grain was influenced by both temperature and moisture content concurrently. The influence of temperature and moisture content on the drying rate ratio exhibits a pattern of increase followed by decrease. These analytical findings offered a novel theoretical foundation and method for strategically adjusting drying condition parameters based on the material's drying state, aiming to achieve efficient and energy-saving drying processes.

It is evident from the comparison of Figure 4a,b and Figure 5a,b that the free energy consumption of the material system was less affected by temperature and moisture content when the moisture content of rice grain exceeded 25% than by the free energy coefficient, water activity, and drying rate ratio. In a high-moisture state, the material has a water activity close to 1. This high water activity provides a strong driving force for water removal, making the drying process less dependent on temperature increases. During the falling rate

drying stage, with water activity below 1 (for example, in the moisture content range of 25% d.b. to 10% d.b., as shown in Figure 5b), temperature and moisture content had a larger impact on free energy consumption compared to the free energy coefficient, water activity, and drying rate ratio. Moreover, all these factors displayed nonlinear characteristics. At this stage, the drying process can be strengthened by increasing the drying temperature, which can considerably increase the free energy, water activity, and drying rate ratio while simultaneously reducing the free energy coefficient.

5. Conclusions

This work presents a theoretical solution for the amount of energy required to bind moisture within rice grains. It also demonstrates a strong mathematical relationship between the rate at which rice grains dry and the amount of energy consumed during the evaporation of moisture at different levels of water activity. Consequently, a theoretical assessment of the thermal consumption associated with rice grain drying can be derived under a variety of environmental conditions. In practical applications, this study not only offers an analytical solution for the drying process of rice grains under specific drying conditions but also establishes a theoretical framework to understand how rice grains dry under various external conditions through analytical methods. This study provides a theoretical foundation for future research into objectively evaluating the drying efficiency of rice grains in practical drying operations and for the development of efficiency evaluation standards for energy utilization in scientifically engineered drying equipment systems.

This study revealed the mathematical expression for the free energy ratio consumption during moisture vaporization in the dry matter system. It obtained the specific free energy consumption coefficient and derived the intrinsic characteristic function of the drying rate ratio of paddy. The theory reveals the following facts:

i. The drying process can be quantitatively described by the transfer and conversion of free energy, regardless of the form of water within the material or changes in mechanical parameters.
ii. The intrinsic theoretical drying rate ratio of the material itself is a single-valued function of the material's water activity, with its mathematical expression as follows: $\frac{-\frac{dM}{d\theta}}{(-\frac{dM}{d\theta})_{\max}} = \frac{1}{1-\ln\phi}$. Under isothermal conditions, water activity is a single-valued function of water content, where water content can be expressed as a mass ratio.
iii. Reduced water activity results in an increase in the free energy consumption of water evaporation in paddy, which can be expressed mathematically as $f_g = R_{pn}T(1-\ln\varphi)$.
iv. The coefficient of specific free energy consumption was found to be equal to 1 when the water activity was 1 in a free state. Furthermore, it was observed that when binding energy between moisture and dry matter existed, the water activity was less than 1. The specific free energy consumption coefficient was found to be greater than 1, indicating that the same amount of water vaporized from the paddy consumed $C_z = 1-\ln\phi$ time heat compared to the free state. Its mathematical expression is $C_z = 1-\ln\phi$.

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Nomenclature

M	moisture content on a dry basis, % d.b.
M_e	equilibrium moisture content, % d.b.
M_c	initial moisture content, % d.b.
M_{el}	equilibrium moisture content in the first falling-rate drying stage, d.b.
M_k	limiting moisture content, % d.b.
φ	water activity, decimal
P	water vapor partial pressure, KPa
P_s	saturated vapor pressure, KPa
R_{pn}	characteristic constant of the water evaporation process, kJ/(kg·K)
C_p	specific heat capacity of water vapor at constant pressure, kJ/kg
f	specific free energy consumption during the vaporization of free-state water, kJ/kg
C_{pi}	specific heat values at different pressures under isothermal conditions, kJ/kg
C_z	specific free energy consumption coefficient
T	moisture vaporization temperature, K
t	Kelvin temperature, K
θ	drying time, hours

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