University of São Paulo
“Luiz de Queiroz” College of Agriculture

Description of grains hydration kinetics and its enhancement using the ultrasound technology

Alberto Claudio Miano Pastor

Dissertation presented to obtain the degree of Master in Science. Area: Food Science and Technology

Piracicaba
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CONTENTS

RESUMO

Descrição e melhoramento da cinética de hidratação de grãos usando a tecnologia do ultrassom

O presente trabalho teve como objetivo estudar o processo de hidratação de grãos e sua possível melhora usando a tecnologia do ultrassom. Estudou-se a cinética de hidratação de diferentes grãos (tremoço andino, feijão Adzuki, grãos de sorgo e grãos de milho) correlacionando a morfologia com modelos matemáticos e os mecanismos de transferência de massa. Também foi estudado o efeito da temperatura e o conteúdo de umidade inicial do grão para complementar a descrição deste processo. Estudou-se a aplicação do ultrassom no processo de hidratação descrevendo-se os possíveis mecanismos (efeito diretos e indiretos) que melhoram a transferência de massa. Como resultado, foi estabelecida a forma como a água entra nos grãos estudados, demostrando que a transferência de água dentro dos grãos é um fenômeno complexo e que acontece por difusão e capilaridade. Foram propostos e utilizados modelos matemáticos apropriados para explicar os processos, descrevendo os parâmetros de acordo com a morfologia dos grãos e os mecanismos de transferência de massa. Ainda, determinou-se como o ultrassom melhora a transferência de massa e em que condições do processo acontecem os efeitos diretos (fluxo inercial e efeito esponja) e efeitos indiretos (formação de micro canais pela cavitação acústica), maximizando o efeito dessa tecnologia. Finalmente, demonstrou-se que a tecnologia do ultrassom melhora o processo de hidratação de grãos de milho, diminuindo significativamente o tempo do processo em cerca de 35 % sem alterar as propriedades térmicas, reológicas e estruturais do seu amido. Como conclusão, o presente trabalho melhorou a descrição de como os grãos são hidratados, demonstrando que o ultrassom pode ser usado para melhorar o processo de hidratação de grãos sem alterar os seus principais produtos industriais. Ressalta-se que os resultados obtidos são desejáveis tanto do ponto de vista acadêmico quanto industrial.

Palavras-chave: Hidratação; Reidratação; Operações unitárias; Transferência de massa; Ultrassom; Novas tecnologias; Engenharia de processos

ABSTRACT

Description of grains hydration kinetics and its enhancement using the ultrasound technology

The present work had as objective to study the hydration process of grains and its possible enhancement using the ultrasound technology. For that, it was studied the hydration kinetics of different grains (Andean lupin, Adzuki beans, sorghum grains and corn kernels) correlating the morphology with mathematical models and the mass transfer mechanisms. Moreover, the effect of the soaking water temperature and the grain initial moisture content were studied to complement the description of this process. The ultrasound application was studied for improving the hydration process, describing the possible mechanisms (direct and indirect effects) that improve the mass transfer process. Therefore, it was established the way by how water enters in the studied grains, demonstrating that the water transfer into the grains is a complex phenomenon and takes place not only due to diffusional mechanisms, but also by capillarity. In addition, suitable mathematical models were proposed and used to explain the processes, describing their parameters according to the grains morphology and the mass transfer mechanisms. Further, it was determined how ultrasound enhances the mass transfer and in which conditions the direct (inertial flow and sponge effect) and the indirect effects (micro channels formation by acoustic cavitation) take place in the process, maximizing the effect of this technology. Finally, it was demonstrated that the ultrasound technology enhanced the hydration process for corn kernels, reducing significantly the process time in approximately 35 %, without modifying the thermal, structural and rheological properties of their starch. In conclusion, the present work improved the description of the grain hydration phenomenon and proved that the ultrasound technology can be used to enhance this process without changing its main industrial component. It is highlighted that the obtained results are thus high desirable for both the industrial and academic point of view.

Keywords: Hydration; Rehydration; Unit operations; Mass transfer; Ultrasound; Novel technologies; Process engineering

RESUMEN

Descripción y mejoramiento de la cinética de hidratación de usando la tecnología de ultrasonido

La presente investigación tuvo como objetivo estudiar el proceso de hidratación de granos y su posible mejora usando la tecnología del ultrasonido. Para lo cual, se estudió la cinética de hidratación de diferentes granos (Tarwi, frejol Adzuki, granos de sorgo y granos de maíz) correlacionando la morfología de ellos con modelos matemáticos y mecanismos de transferencia de materia. Además, se estudió el efecto de la temperatura del agua de remojo y el efecto del contenido de humedad inicial de los granos para complementar la descripción del proceso. Asimismo, se estudió la aplicación del ultrasonido para mejorar el proceso de hidratación, describiendo los posibles mecanismos (efectos directos e indirectos) que mejoran la transferencia de materia. Como resultado, se comprobó que la forma como el agua entra en los granos es un fenómeno complicado que se lleva a cabo no sólo por difusión, sino también por capilaridad. Además, se usaron y propusieron modelos matemáticos apropiados para explicar el proceso, describiendo sus parámetros de acuerdo a la morfología de los granos y los mecanismos de transferencia de materia. Al mismo tiempo, fue determinado como el ultrasonido mejora la transferencia de materia y en qué condiciones del proceso actúan los efectos directos (flujo inercial y efecto esponja) y efectos indirectos (formación de micro canales por la cavitación acústica), maximizando el efecto de dicha tecnología. Finalmente, se demostró que la tecnología de ultrasonido mejora el proceso de hidratación de los granos de maíz reduciendo significativamente el tiempo del proceso aproximadamente en un 35 %, sin modificar las propiedades térmicas, reológicas y estructurales de su almidón. En conclusión, la presente investigación mejoró la descripción de proceso de hidratación de granos y demostró que la tecnología del ultrasonido puede ser usado para mejorar el proceso sin alterar los principales componentes de los granos. Cabe resaltar que los resultados son muy deseados tanto desde el punto de vista industrial como el académico.

Palabras clave: Hidratación; Rehidratación; Transferencia de materia; Ultrasonido; Nuevas tecnologías; Ingeniería de procesos

FIGURE LIST

TABLE LIST

SYMBOL LIST

CHAPTER 1

a,b = parameters of model fit evaluation (eq. (1.10)) [different units]

a_w = water activity (eq. (1.11))

A = area of diffusion (eq. (1.4)) [m^2]

A,B = parameters of the Oswin Model (eq. (1.11)) [different units]

C = concentration of a component (A or B) (eq. (1.4), eq. (1.5) and eq. (1.7)) [kg/m3]

D = mass diffusivity (eq. (1.4) and eq. (1.5)) [m^2/s]

E = elasticity (eq. (1.1)) [Pa]

f = frequency (eq. (1.2)) [kHz]

g = gravity acceleration (eq. (1.6)) [m/s^2]

h = distance the fluid is drawn into the capillary (eq. 6) [m]

I = transducer intensity (eq. (1.3)) [W]

k_L, k_{P1}, k_{P2}, P_1,P_2, k_{H1}, k_{H2}, k_1, k_2, α, β, k_{I0}, k_{I1} = kinetic parameters of the most used mathematical models to describe the food hydration with downward concave shape behaviour (Table 1.1) [different units]

k_K, τ = kinetic parameters of the Kaptso et al. (2008) model (Table 1.2, food hydration with sigmoidal shape behaviour) [different units]

k_{IA} = kinetic parameters of the Ibarz and Augusto model (2014) (Table 1.2, food hydration with sigmoidal shape behaviour) [$(\%_{d.b.}\cdot min)^{-1}$]

k_m = mass transfer coefficient (eq. (1.7)) [$m^3/m^2\cdot s$ or m/s]

$\dot{m}_B$ = mass flux of the component B (eq. (1.4)) [kg/s]

M = product moisture content on dry basis [g water / 100 g solids = $\%_{d.b.}$]

M_0 = initial moisture content [g water / 100 g d.b.]

$M_{experimental}$ = Experimental moisture content value (eq. (1.8), eq. (1.9) and eq. (1.10)) [% d.b.]

M_{model}= Model moisture content value (eq. (1.8), eq. (1.9) and eq. (1.10)) [% d.b.]

M_∞ = equilibrium moisture content [g water / 100 g d.b.]

N_A = mass flux (eq. (1.7)) [kg/s.m^2]

$NRMSD$ = normalized root-mean-square deviation values (eq. (1.9)) [$\%_{exp}$]

$RMSD$ = root-mean-square deviation values (eq. (1.8)) [g water / 100 g d.b.]

P_a = acoustic pressure (eq. (1.2)) [Pa]

P_{amax} = maximum pressure of wave amplitude (eq. (1.2)) [Pa]

r = radius of a capillary [m] (eq. (1.6))

t = time [min]

T = temperature [ºC]

T_K = absolute temperature [K]

η = viscosity [Pa.s] (eq. (1.6))

ρ = density [kg/m^3] (eq. (1.1))

θ = contact angle between the fluid and the capillary fluid [rad] (eq. (1.6))

v = sound velocity [m/s] (eq. (1.1))

γ = surface tension of a fluid [N/m] (eq. (1.6))

CHAPTER 2

a = Linear model parameter (slope) (eq. (2.3)) [Different unit]

b = Linear model parameter (ordinate axis intercept) (eq. (2.3)) [Different unit]

k_{IA} = Ibarz-Augusto's kinetics parameter related to the lag phase and water absorption rate (eq. (2.5) and eq. (2.9)) [g/100g d.b.-1·min-1]

k_K = Kaptso et al. kinetics parameter related to water absorption rate (eq. (2.4) and eq. (2.8)) [g/100g d.b.-1]

M_{eq} = Equilibrium moisture content (eq. (2.4), eq. (2.5), eq. (2.6) and eq. (2.7)) [g/100g d.b.]

$M_{experimental}$ = Experimental moisture content value (eq. (2.13) and eq. (2.14)) [g/100g d.b.]

M_{model} = Model moisture content value (eq. (2.13) and eq. (2.14)) [g/100g d.b.]

M_o = Initial moisture content (eq. (2.5)) [g/100g d.b.]

M_t = Moisture content in time t (eq. (2.4) and eq. (2.5)) [g/100g d.b.]

$M(t,T)$ = Moisture content in time t and temperature T (eq. (2.11) and eq. (2.12)) [g/100g d.b.]

$NRMSD$ = Normalized root-mean-square deviation values (eq. (2.2)) [%exp]

R = Constant of the ideal gases (eq. (2.8), eq. (2.9) and eq. (2.10) [= 8.314 J·mol-1·K]

$RMSD$ = Root-mean-square deviation values (eq. (1)) [g/100g d.b.]

T = Temperature (eq. (2.6), eq. (2.7), eq. (2.8), eq. (2.9), eq. (2.10), eq. (2.11) and eq. (2.12)) [K]

t = Time (eq. (2.4), eq. (2.5), eq. (2.11) and eq. (2.12)) [min]

τ = Kaptso et al. kinetics parameter related to lag phase (eq. (2.4) and eq. (2.10)) [min-1]

Wo = Initial weight [g]

Wt = Weight in time t [g]

CHAPTER 3

a = linear model parameter (slope) (eq. (3.5)) [Different unit]

A and B = parameters of Oswin Model (eq. (3.3)) [Different unit]

b = linear model parameter (ordinate axis intercept) (eq. (3.5)) [Different unit]

k_1 and k_2 = Peleg's Model parameters (eq. (3.2)) [Different unit]

k_K = Kaptso et al. kinetic parameter related to water absorption rate (eq. (3.1), and eq. (3.8)) [% d.b.-1]

M = Moisture content (eq. (3.6) and eq. (3.7)) [% d.b.]

M_{eq} = Equilibrium moisture content (eq. (3.1)) [% d.b.]

$M_{experimental}$ = Experimental moisture content value (eq. (3.3), eq. (3.4), eq. (3.5) and eq. (3.11)) [% d.b.]

M_{model}= Model moisture content value (eq. (3.3), eq. (3.5) and eq. (3.11)) [% d.b.]

MN = moisture content of the grain in equilibrium with the environment [14.96 % d.b.]

M_o = Initial moisture content (eq. (3.2), eq. (3.8), eq. (3.9) and eq. (3.10)) [% d.b.]

M_t = Moisture content in time t (eq. (3.1) and eq. (3.2)) [% d.b.]

$M(t,T)$ = Moisture content in time t and temperature T (eq. (3.10)) [% d.b.]

$NRMSD$ = normalized root-mean-square deviation values (eq. (3.4)) [%exp]

$RMSD$ = root-mean-square deviation values (eq. (3.3)) [% d.b.]

t = Time (eq. (3.1), eq. (3.2) and eq. (3.10)) [min]

τ = Kaptso et al. kinetic parameter related to lag phase (eq. (3.1) and eq. (3.9)) [min-1]

1 INTRODUCTION

Grain production is an important entry in the world since it is very important for the food industry and human alimentation and nutrition. There is a huge diversity of them that can provide protein, lipids, carbohydrates (starch, fiber), vitamins, minerals, additives, etc. After they are harvested, they have to pass through different process like cleaning, selection, classification, hydration, cooking, extraction and packaging before they are used.

This research work was focused on explaining and improving the grain hydration process. This process consists in soaking the grains in water in order to increase their moisture content. Thus, it facilitates the next processes like extraction (starch, phenols, protein, etc.), cooking (by reducing time), germination (activating enzymatic activity and physiological process) and fermentation (increase water activity). However, this process is very slow, taking around 6 to 20 hours depending of grain size, morphology and composition. Therefore, in order to reduce this time, traditional approaches can be applied, such as using high temperatures. However, by using high temperatures, there are important changes on the grain´s nutritional and textural properties. Further, a high amount of energy is required.

On the other hand, there are different novel technologies that can reduce the soaking time and enhance the process. For example, the ultrasound technology was successfully used in many kind of processes in food industry. However, there are still few researches using this technology to enhance the hydration process. In addition, the mechanisms that improve the process by ultrasound technology have not been demonstrated yet.

The present dissertation is being presented in chapters to have a better organization of the results (Figure 1.1).

First at all, in the Introduction is presented the Literature Review, which contents the basics definitions to understand the present work. Next, the results are presented in four Chapters, which are divided in two parts. The first part consists on the **Grain hydration process description**, where it was studied the effect of temperature and initial moisture content on the hydration kinetics, and the water entrance pathway in two different grains: Andean lupin (*Lupinus mutabilis* Sweet; Chapter 2) and Adzuki beans (*Vigna Angularis*; Chapter 3*)*.The Andean lupin was selected due to its high protein content which it is important on human and animal nutrition. The Adzuki beans was used due to the special hydration behavior that they have shown in previous research works.

The second part consist of explaining the **Ultrasound effect on the grain hydration process,** where was firstly studied how the ultrasound enhances the mass transfer phenomena (Chapter 4) and then, how ultrasound enhance the hydration process of corn kernels (Chapter 5). In the Chapter 4, two different food were used: sorghum grains and yellow melon cylinders (low and high water activity food). Corn kernels were used in Chapter 5 because of their importance in industry. This cereal is very important due to its starch, which it is used in many kind of products.

Finally, the last chapter presents the general conclusions of all the presented research work, as well as suggestions for future studies.

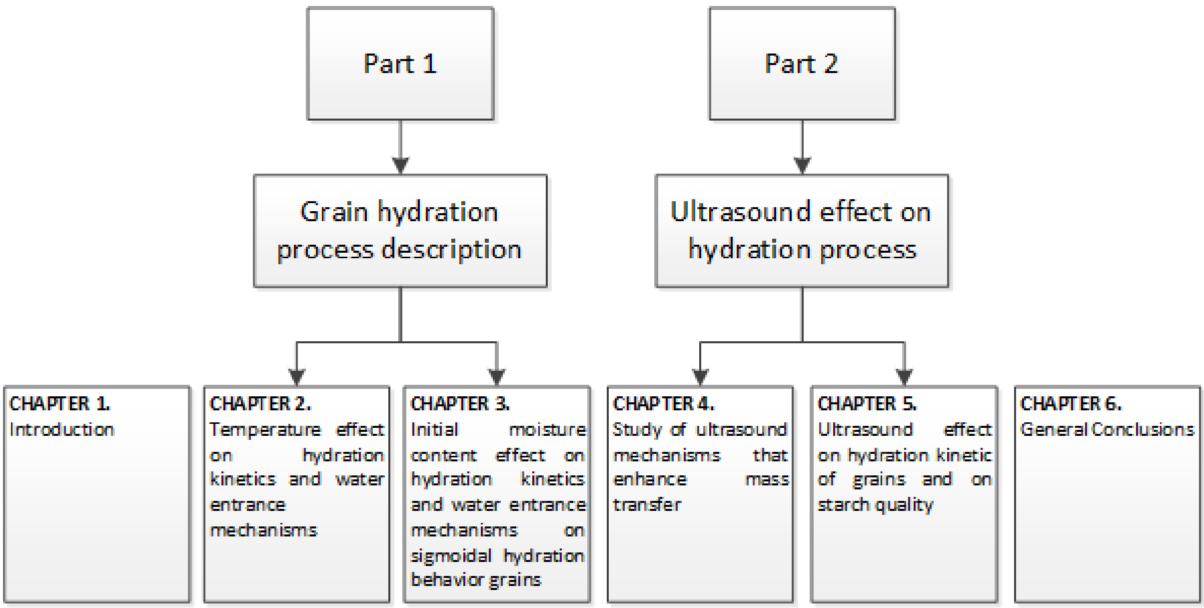

Figure 1.1 – Schematic diagram explaining the Dissertation Organization

1.1 Hydration of grains

The hydration, especially of previous dehydrated food, is a complex process to restore the initial food properties. The great variety of dehydrated food and the concern of fulfilling the quality specifications and energy conservation, emphasizes the need for a thorough understanding of the process of rehydration (LEE; FARID; NGUANG, 2006). Hydration or water soaking of dried food like grains is a crucial step in the industrialization process and provides a number of beneficial effects on physicochemical and nutritional quality (BORDIN et al., 2010; CARMONA-GARCÍA et al., 2007; DRUMM et al., 1990; HUMA et al., 2008; YASMIN et al., 2008)

The soaking process is widely used in different grains processing due to many reasons, as hydration is necessary for processes like cooking, extraction, fermenting, germinating and eating. During soaking, the grains cellular wall is hydrated and the enzymes start to hydrolyze pectin and others polysaccharides. The activation of those enzymes has shown a significant reduction of thermal treatment time needed to achieve optimum texture (JOSHI et al., 2010; MARTÍNEZ-MANRIQUE et al., 2011; PUJOLÀ; FARRERAS; CASAÑAS, 2007). In some of the soaking industrial applications, the grains must be grinded by the wet milling process (BELHADI et al., 2013; ZHAN et al., 2006), in special before the starch extraction. Further, the gelatinization process of grain starch (TURHAN; SAYAR; GUNASEKARAN, 2002) needs water for the hydration of amylose and amylopectin and its dispersion on aqueous medium (DERGAL, 2006). Moreover, water is distributed by presented proteins in grains which help denaturation process during cooking (ABU-GHANNAM, 1998a, 1998b; DESHPANDE; BAL, 2001), also enhancing palatability and digestibility, reducing cooking time (SEYHAN-GURTAS; AK; EVRANUZ, 2001), improving the nixtamalization process (FERNÁNDEZ-MUÑOZ et al., 2011), and helping the germination process by the activation of metabolic processes in the seed (CERRILLO, 2003). Therefore, it is important to understand the hydration kinetics of different food products, as well as the influence of process conditions on its rate.

In soaking process, it was thought that water penetrates the seed coat, crossing the cotyledons or endosperm and reaching the center of seeds. However, this process is not as simple as previously thought due to the complex morphology of the grains. It is necessary to characterize and optimize hydration process in order to improve the process by increasing its rate. The evaluation and modeling of moisture content during grain soaking have been widely studied, considering the effect of different process conditions such as the temperature (ABU-GHANNAM, 1998a; ABU-GHANNAM; MCKENNA, 1997; FERNÁNDEZ-MUÑOZ et al., 2011; JIDEANI; MPOTOKWANA, 2009; KAPTSO et al., 2008; KASHIRI; KASHANINEJAD; AGHAJANI, 2010; KHAZAEI; MOHAMMADI, 2009; MASKAN, 2001; OLIVEIRA et al., 2013; PIERGIOVANNI, ANGELA ROSA, 2011; PIERGIOVANNI; ANGELA; SPARVOLI; ZACCARDELLI, 2012; SOLOMON, 2009). Recently, novel technologies were also proposed in order to increase the grains hydration rate, such as the high pressure processing (IBARZ; GONZÁLEZ; BARBOSA-CÁNOVAS, 2004) and the ultrasound technology (GHAFOOR et al., 2014; PATERO; AUGUSTO, 2015; RANJBARI et al., 2013; ULLOA et al., 2015; YILDIRIM; ÖNER; BAYRAM, 2013).

Through the time, it has been obtained many models to explain the hydration behavior of grains (downward concave shape (DCS) behavior and sigmoidal behavior (Figure 1.2) (Table 1.1 and Table 1.2). The DCS behavior is characteristic by a high hydration rate at the beginning of the process. This hydration rate decreases until reaching the equilibrium moisture when it becomes zero. In contrast, the sigmoidal behavior starts with a very slow hydration rate, then it increases until some inflexion time when it starts to decrease again until reaching the equilibrium moisture.

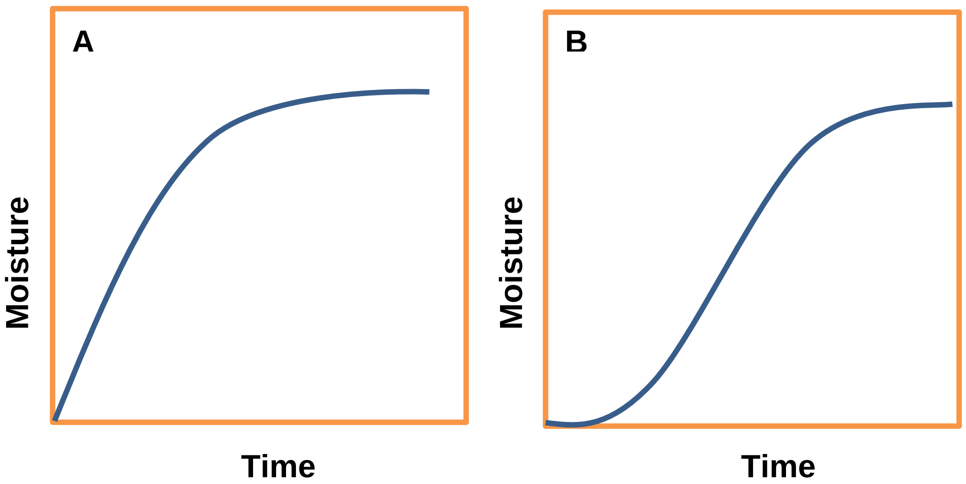

Figure 1.2 – Common hydration curve of grain: A. downward concave shape behavior (DCS) and B: sigmoidal behavior

Many mathematical models were used to explain both behavior. They are showed in Table 1.1 and Table 1.2.

Table 1.1 – Mathematical models to describe the food hydration with downward concave shape behavior

Model	Equation	Reference
Lewis (first order kinetics)	$\frac{M(t)-M_\infty}{M_o-M_\infty}=\exp(-k_L\cdot t)$	(LEWIS, 1921)
Page	$\frac{M(t)-M_\infty}{M_o-M_\infty}=\exp(-k_{P1}\cdot t^{k_{P2}})$	(PAGE, 1949)
Henderson	$\frac{M(t)-M_\infty}{M_o-M_\infty}=P_1\cdot\exp(-k_{H1}\cdot t)+P_2\cdot\exp(-k_{H2}\cdot t)$	(HENDERSON, 1974)
Peleg	$M(t)=M_0+\frac{t}{k_1+k_2\cdot t}$	(PELEG, 1988)
Weibull	$\frac{M(t)}{M_\infty}=1-\exp\left[-\left(\frac{t}{\alpha}\right)^\beta\right]$	(SAM SAGUY; MARABI; WALLACH, 2005)
Ibarz-González-Barbosa-Cánovas	$M(t)=\frac{k_{I0}}{k_{I1}}-\left(\frac{k_{I0}}{k_{I1}}-M_0\right)\exp\left(-k_{I1}\cdot t\right)$	(IBARZ et al., 2004)

Table 1.2 – Mathematical models to describe the food hydration with sigmoidal shape behavior

Model	Equation	Reference
Kaptso-Njintang-Komnek-Hounhouigan-Scher- Mbolung	$M(t)=\frac{M_\infty}{1+\exp\left[-k_K\cdot(t-\tau)\right]}$	(KAPTSO et al., 2008)
Ibarz-Augusto	$M(t)=\frac{M_\infty}{1+\frac{M_\infty-M_0}{M_0}\exp\left(-k_{IA}\cdot M_\infty\cdot t\right)}$	(IBARZ; AUGUSTO, 2015)

The effect of temperature on the grains hydration kinetics is the most studied approach to accelerate the process rate. The general behavior is that the higher the temperature of hydration process is, the higher the water absorption rate is. The temperature causes the increase of the water uptake because of some factors like reduction of water viscosity, increment of porous size by dilatation, decreasing of the compactness, etc. On the other hand, the maximum equilibrium moisture, according to some researches (Table 1.3), can increase, decrease or not to change with the increment of temperature. The increment of the equilibrium moisture was explained by different authors. It is caused because of the dilatation of the grain, partial degradation of pectin and solubility of cell wall polysaccharides. The decrease of equilibrium moistures was observed in some grains, and it happens due to the change of the cell integrity and the quickly grain’s external layer saturation that decreases the mass transfer. In addition, it could happen because the higher temperatures can change the starch and proteins properties by gelatinization and denaturation respectively reducing the water holding capacity. There are few researches where it was found that equilibrium moistures did not change with the increase of temperature, but it was not explained.

Moreover, it is important to highlight that by increasing the process temperature, undesirable reactions can occur during processing, such as protein denaturation, starch gelatinization, and molecular degradation. Further, additional equipment and energy amount are needed in order to heat the whole grain and water amount during hydration, as well as the costs with insulation or energy dissipation to the boundaries during the long period of processing. By this reason, the increase in process temperature is rarely used in the industry, even so resulting in longer processes. Therefore, although the positive effect of heating is well known, there is a need for studying new technologies in order to improve the grain hydration kinetic. In fact, the ultrasound technology was recently proposed in order to achieve that.

Table 1.3 – Researches where it was studied the effect of temperature on hydration kinetic of different grains

Grain		Model	Behavior	M_∞	Author
Phaseolus vulgaris L.	Red Kidney Beans	Peleg	DCS	↓	(ABU-GHANNAM; MCKENNA, 1997)
Cicer arietinum L.	Chickpeas	Peleg	DCS	↓	(GOWEN et al., 2007)
Vigna angularis	Adzuki beans	Kaptso	Sigmoidal	↓	(OLIVEIRA et al., 2013)
Lupinus albus	Roasted Lupin	Peleg	Sigmoidal	↓	(SOLOMON, 2009)
Oryza sativa	Rice	Fick	DCS	↑	(BELLO; TOLABA; SUAREZ, 2004)
Oryza sativa	Rice (Dehusked)	Fick	DCS	↑	(BELLO et al., 2004)
Oryza sativa	Rice (Polished)	Fick	DCS	↑	(BELLO et al., 2004)
Vigna subterranea	Bambara bean	Peleg	DCS	↑	(JIDEANI; MPOTOKWANA, 2009)
Sorghum spp.	Sorghum	Peleg	DCS	↑	(KASHIRI et al., 2010)
Sesamum indicum L.	Sesame seeds	Peleg	DCS	↑	(KHAZAEI; MOHAMMADI, 2009)
Triticum spp.	Wheat	Peleg	DCS	↑	(MASKAN, 2001)
Phaseolus vulgaris	Common bean	Peleg	Sigmoidal	↑	(PIERGIOVANNI, ANGELA ROSA, 2011)
Amaranthus cruentus	Amaranth grain	Fick	DCS	↑	(RESIO; AGUERRE; SUAREZ, 2006)
Voandzeia subterranea	Black Bambara groundnuts	Kaptso	Sigmoidal	↑	(KAPTSO et al., 2008)
Vigna unguiculata	Garoua cowpea	Kaptso	Sigmoidal	○	(KAPTSO et al., 2008)
Vigna unguiculata	West cowpea	Kaptso	Sigmoidal	○	(KAPTSO et al., 2008)
Voandzeia subterranea	White Bambara groundnuts	Kaptso	Sigmoidal	○	(KAPTSO et al., 2008)
Glycine max	Soybean	Hsu	DCS	○	(COUTINHO et al., 2010)

* M_∞ is the equilibrium moisture that it can decrease (↓), increase (↑) or not change (○)

1.2 Ultrasound Technology

The ultrasound is defined as the sound waves which have higher frequency than human can detect (>20 kHz). The upper limit of ultrasonic frequency is one that is not sharply defined but is usually taken to be 5 MHz for gases and 500 MHZ for liquids (MASON; LORIMER, 2002). The ultrasound waves can be transmitted through any substance (solid, liquid and gas), which possesses elastic properties. In fluids (liquid and gases), the movement of the adjoining molecules caused by the sound source takes place in the direction of the wave (longitudinal waves). However, in solids, the movement is perpendicular to the direction of the waves due to solids have shear elasticity supporting tangential stress (Figure 1.3) (MASON; LORIMER, 2002).

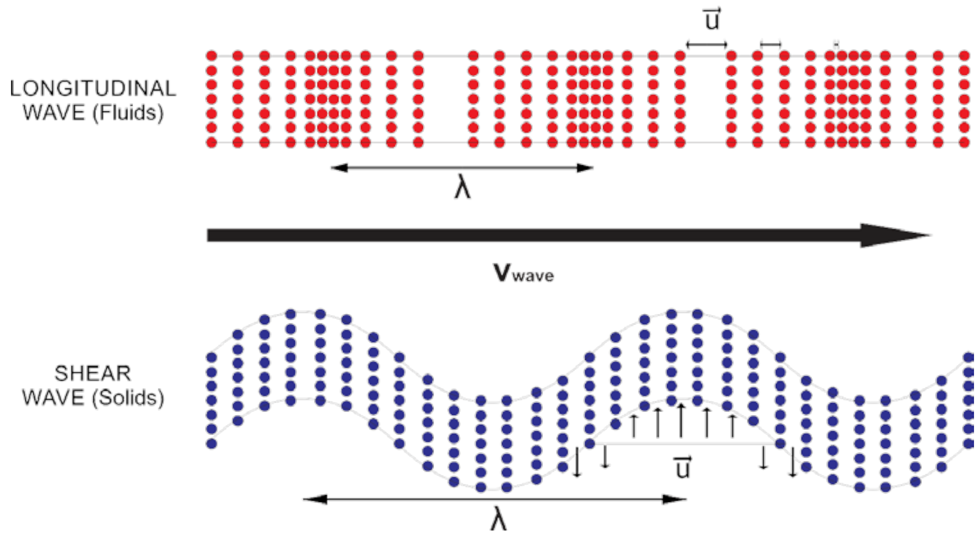

Figure 1.3 – Representation of the movement of adjoining molecules $\vec{u}$ in ultrasound waves. v_{wave} is velocity of sound wave propagation and λ is the sound wave length. Adapted from Gennisson et al. (2013)

For the ultrasound generation it is used a device called transducer. Generally, a transducer is a device that is able to convert one form of energy into another. Ultrasonic transducers are oscillatory systems that convert mechanical or electrical energy into acoustic energy. There are three types: gas-driven, liquid-driven or electromechanical. The most common type is the electromechanical, which uses piezoelectric technology (MASON; PETERS, 2004). It uses ceramics containing piezoelectric materials that they are the heart of the transducer since they convert the electrical energy to acoustic energy (RASTOGI, 2011). The transducer is bonded to a surface that can transmit this vibration through the fluid. The energy transferred to the solution, although inducing mechanical effects, is ultimately turned into heat. In addition, if cooling is not provided, ultrasonic processing will result in temperature increase (KENTISH; FENG, 2014)

There are many types of ultrasonic equipment such as ultrasonic bath, ultrasonic probe, and parallel or radial vibration systems. The ultrasound bath is a tank with transducers bonded to its base. This type of equipment is often used in low power to avoid cavitation damage to the tank wall, and the power density is low due to the large volume of the processing liquid (MASON, 1998). The ultrasonic probe contains one or many shaped metal horns attached to the transducer in order to achieve high power intensity (RASTOGI, 2011).

The ultrasound technology is very used in the food industry in order to enhance the processes, maximize the quality and ensure its safety (KNORR et al., 2011). According to the frequency range, the application of ultrasound in food processing, analysis and quality control is divided in low and high power ultrasound. The low power ultrasound (LPU) is generated with frequencies higher than 100 kHz and intensities lower than 1 W/cm^2, while the high power ultrasound (HPU) is generated with frequencies between 20 and 500 kHz and intensities higher than 1 W/cm^2 (AWAD et al., 2012).

In LPU, sound is propagated through the food like mechanic waves causing disruptions by the compression and decompression. Those ultrasonic waves are characterized by their wave length, frequency, pressure and period. The velocity is determined by the product of the frequency and wave length, which it means that high frequency waves have short wave length and vice versa. The velocity (v) of the sound propagation is determined by the medium density (ρ) and elasticity (E) according to Newton-Laplace equation (BLITZ, 1963, 1972):

$$v = \sqrt{\frac{E}{\rho}} \tag{1.1}$$

This equation implies that the ultrasound velocity is higher in solid bodies than in liquids. The interaction between sound waves and matter alters the sound velocity and attenuates sound waves by absorption and or dispersion mechanisms (MCCLEMENTS, 1995). In food analysis, since ultrasound velocity is very sensible to molecular organization and intermolecular interaction, its measurement allows the determination of composition, structure, physical state and several molecular processes (BUCKIN; KUDRYASHOV; O'DRISCOLL, 2002, 2003).

The low power ultrasonic waves are used for analysis and noninvasive monitoring of many materials during their process and storing in order to ensure the high quality and safety. It is also used for the quality control of fresh vegetables during pre and post-harvest, cheese, cereals, emulsified lipids, food gels, frozen food and so on. Another important application is the detection of adulterations (AWAD et al., 2012). In meat industry, low power ultrasound allows to obtain ultrasonic vibration – reflection images, which they scan live animal internal tissues and organs helping to determine composition of meat and fat before they are slaughtered (FAULKNER et al., 1990). Based on the ultrasound velocity behavior at different temperatures, it can be accurately predicted the ratio of lean tissue, fat, moisture and protein of meat products (SIMAL et al., 2003). Moreover, LPU has been used in order to determine sugar content of fruit juices and beverages, giving a well linear fitting with sugar content (°Brix) and, additionally, an exponential fitting with viscosity (AWAD et al., 2012).

In the high power ultrasound (HPU), the parameters energy power, intensity, pressure, velocity and time are important to be evaluated. The variation of pressure due to the HPU can be described using the following equation (PATIST; BATES, 2008):

$$P_a = P_{amax}.\sin(2\pi f t) \tag{1.2}$$

Where P_a is the acoustic pressure (sinusoidal wave), which depends on time (t), frequency (f) and the maximum pressure of wave amplitude. The P_{amax} value is related to the input power or transducer intensity (I):

$$I = P_{amax}/2\rho v \tag{1.3}$$

Where ρ is the medium density and v is the sound velocity in the medium (MUTHUKUMARAN et al., 2006). Higher intensities (low frequencies) induce acoustic cavitation (MASON, 1998).

When food is subjected to an ultrasonic process, the mechanical waves travel causing compression and expansion cycles. In expansion cycles, the food internal pressure decreases overcoming the intermolecular forces which causes micro bubbles formation due to its vaporization. On the other hand, in the compression cycles, the food internal pressure increases, so the micro bubbles, previously formed, begin to condensate. The collapse of these bubbles, or cavitation, is a process that involves great energy and shear, being the principle of using this technology in food.

In fact, it is believed that the main ultrasound actions on food process are due to cavitation and enhancement of the mass transfer phenomena (CHEMAT; KHAN, 2011). The different ways in which cavitation can be beneficially used in food process are the reduction of reaction time, reaction yield increment and less use of high temperatures or pressures (MCCLEMENTS, 1995). During the cavitation, the water molecules can form free radicals, which intensify chemical reactions, induce protein molecules crosslinking in aqueous medium (CAVALIERI et al., 2008) and enhance mass transfer due to generation of local turbulent micro-circulation (acoustic current) (GOGATE; PANDIT, 2011).

Cavitation is affected by frequency and intensity of ultrasound. Higher frequencies decrease the cavitation bubbles formation because it needs more power to maintain the same cavitation conditions at high frequencies than using low frequencies. When frequency increases to the order of MHz, cavitation is very difficult to produce because the rarefaction and compression cycle is extremely short. The formation of cavitation needs a finite time to appear, so the very short rarefaction (decompression) cycle made impossible its appearance (MASON; TIMOTHY; PETERS, 2004; YILDIRIM et al., 2013). At low frequencies, the intensities required are small (in air-saturated water the value is about 1 W/cm^2 at 20 kHz). A considerably higher intensity is necessary to obtain cavitation at higher frequencies (MASON; LORIMER, 2002).

The use of ultrasound can improve the quality of different food during its process (MASON; PANIWNYK; LORIMER, 1996). The mechanical effect has many applications such as flavor extraction, degassing, foam breaking, emulsification and enhancing of crystallization (HIGAKI et al., 2001). The chemical and biochemical effects are useful tools to sterilize equipment, to prevent food spoilage and to remove pathogen bacteria and bacterium biopolymers (BAUMANN; MARTIN; FENG, 2009). Other applications of HPU are sonocristalization, defoaming, enzymatic inactivation, microbial inactivation, drying, ultrasonic assisted extraction, and so on (AWAD et al., 2012).

The ultrasound technology offers plenty of advantages in terms of productivity, yield and selectivity, improving the process time, improving the quality, reducing the chemical and physical risks and protecting the environment. The simplicity, portability and the low cost make this technology an essential element in research laboratories, pilot plants and big food processing companies. In addition, since ultrasound maximized the production while energy is saved, it has been considered as a green technology with many promising expectations in technology and food engineering (AWAD et al., 2012). In fact, it is proven as a useful tool in different mass transfer processes.

1.3 Mass transfer phenomena on food processing

In mass transfer operations, the transport of the components take place by molecular or convection mechanisms, which imply the movement of a component's molecules from the point of high activity to the low activity (which in many cases can be simplified by the concentration). In other words, the transfer is carried out by the concentration gradient, and, when concentration equilibrium is reached, the mass transfer stops (IBARZ; BARBOSA-CANOVAS, 2014). In food processing, mass transfer phenomena are present in hydration, freeze-drying, osmotic dehydration, salting or desalting, curing and pickling, extraction, smoking, baking, frying, drying of foods, membrane separations, and the transmission of water vapor, gases, or contaminants across a packaging film (WELTI-CHANES; VELEZ-RUIZ, 2002).

Mass transfer can involve molecular scale mass diffusion and bulk transport of mass due to convection flow (SINGH; HELDMAN, 2014). Further, other mass transfer mechanisms can be important in food processing, such as the capillarity (AGUILERA; MICHEL; MAYOR, 2004).

The diffusion process can be described mathematically using the Fick's Law:

$$\frac{\dot{m}_B}{A} = -D\frac{\partial c}{\partial x} \tag{1.4}$$

Mass transfer in three dimensional Cartesian co-ordinates (x, y and z) is given by:

$$\frac{\partial C}{\partial t} = D\left[\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right] \quad (1.5)$$

Where $\dot{m}_B$ is mass flux of the component B (kg/s); C is the concentration of B (kg/m^3); D is the mass diffusivity (m^2/s) of the component B ; A is the area of diffusion (m^2) and t is the time (s).

The analytical solution of eq. (1.5) for complex shapes, initial and boundary conditions is complex. However, there are solutions for some regular geometries like infinite slab, cylinder and sphere (CRANK, 1979). By using these equations, the effective diffusion coefficient (D_{eff}) can be obtained by plotting experimental data in the form of log against time (ROUSSEAU, 1987). It is important to highlight that the parameter D_{eff} represents all possible forms of mass transfer involved in the process, not only diffusional ones. A major drawback of this is that no efforts have been made to resolve microstructural aspects to understand the mechanism that mass transfer involves (AGUILERA; STANLEY, 1999). For that, since food are structurally complex, the D_{eff} almost never fits experimental data (AGUILERA et al., 2004).

Many kinds of solid food have porous microstructure that are known as capillaries when their diameter is less than 10^{-7} m and porous when their diameter is higher (MITTAL, 2010). They cause capillary penetration of a liquid into the pore spaces that is usually viewed as a spontaneous process driven by interfacial pressure differences (AGUILERA et al., 2004; HAMRAOUI; NYLANDER, 2002). This phenomenon contributes to the mass transfer, helping the transport of fluids inside the food matrix and was proven to be important in many situations such as rehydration (CUNNINGHAM et al., 2008; SAM SAGUY et al., 2005; WALLACH; TROYGOT; SAGUY, 2011), fat migration (AGUILERA et al., 2004) and water migration in gels (STEVENSON; DYKSTRA; LANIER, 2013). The capillary rise of a finite liquid throughout a cylinder channel follows the Lucas-Washburn equation (KROTOV; RUSANOV, 1999):

$$\frac{2}{r}\gamma\cos\theta = \frac{8}{r^2}\eta h\frac{dh}{dt} + \rho g h \quad (1.6)$$

Where h is the distance the fluid is drawn into the capillary; γ is the surface tension of the fluid; θ is the contact angle between the fluid and the capillary fluid; r is the radius of the capillary; ρ and η are the density and viscosity of the liquid respectively; and g is the gravity acceleration.

Therefore, the mechanisms of liquid water transfered in porous solid food can be classified as: diffusion in solid phase, liquid diffusion in pores, surface diffusion of absorbed water, capillary flow when capillaries are filled with water and hydraulic flow pores (MITTAL, 2010).

Mass can also be convectively transfer due to bulk motion created by turbulence. Molecular diffusion still exists, but with a small contribution (MITTAL, 2010). Convective mass transfer only occurs in liquid and gases, and within the structure of a porous solid. The convective mass transfer coefficient k_m ($m^3/m^2 \cdot s$ or m/s) is defined as the rate of mass transfer per area unit per concentration unit (SINGH; HELDMAN, 2014). It is convenient to express the transfer flux for a component according to the following expression:

$$N_A = k_m(c_{A1} - c_{A2}) \tag{1.7}$$

Where N_A is the mass flux, k_m is the mass transfer coefficient and $(c_{A1} - c_{A2})$ is the concentration difference of the component A.

Due to convective mass transfer coefficient is difficult to measure, it is used a global coefficient. In the mathematical treatment of global transfer, the denominated double film theory is usually applied, in which it is assumed that at both sides of the interphase, there is a stagnant film that offers true resistance to the transfer of the considered component (IBARZ; BARBOSA-CANOVAS, 2014). The mass transfer in the phases can be expressed as follows:

$$N_A = k_{Aj}(C_{Aj} - C_{Aj}^{i}) \tag{1.8}$$

Where N_A is the mass flux, k_{Aj} is the mass transfer coefficient in phase j and C_{Aj} is the concentration of component A in the bulk of phase j. The superscript i means the concentration in the interphase.

The exact mechanism of mass transfer is still unknown for most of the food processes. Despite all of them can take place simultaneously in the process, simplifications can be considered in order to study specific processes.

Several unit operations commonly applied in food processing are based on the mass transfer phenomena, such as drying, osmotic dehydration, salting, extraction, filtration, distillation, hydration and acidification processes. Some examples of studies regarding the mass transfer in food processing are presented as follow.

The Fick's second law of diffusion was used to describe rehydration kinetics of potato cylinders at 20 and 80°C (CUNNINGHAM et al., 2008). The process was characterized by two effective diffusion coefficients (two stages) which were dependent of temperature (interpreted by the Arrhenius equation), solid-liquid ratio, sample dimensions and presoaking step (with ionic surfactants and NaCl). Agitation and non-ionic surfactants did not affect the rehydration process. The rehydration ratio increased with increasing solid-to-liquid ratio (up to 1:50); however, agitation had negligible effect on the behavior. The rehydration kinetics increased with decreasing sample diameter and increasing sample area (CUNNINGHAM et al., 2008).

The drying characteristics of broccoli were studied in a convective dryer using constant air velocity of 2 m/s and air temperature of 60°C (DOYMAZ, 2013). It was observed that the drying rate was increased by the blanching temperature, but any possible explanation of that was reported. In fact, it is probable that the enhancement was due to the cell integrity. The data were fitted in twelve drying models and drying constants and coefficients were determined by nonlinear regression analysis. Fick's Second Law was used to calculate the effective moisture diffusivity, which varied from 1.987 $x10^{-8}$ to $3.577x10^{-8}$ m^2/s for the given blanching temperature range.

Mass and heat transfer coefficients during pear convective drying were determined (DA SILVA et al., 2013). For drying, it was used two pear varieties that were molded in the form of a cylinder. Drying was performed in a forced air oven at the temperatures of 68, 76, 84 and 92°C for blanched and unblanched samples. Those authors reported that the heat and mass transfer coefficients varied linearly with temperature and that both were very dependent on boundary limit conditions, which were influenced by geometry of the surface, method of fluid movement and by a series of thermodynamic and fluid transport properties

The mass transfer kinetics during osmotic dehydration of pumpkins was modeled by assuming Fickian diffusion of sucrose and water in unsteady state conditions (ABRAÃO et al., 2013). It was observed that water and sucrose effective diffusions coefficients increase significantly with the temperature increment.

Significant increase in the effective water diffusivity and decrease in the sucrose effective diffusivity was observed when the sucrose solution concentration increased from 40°Brix to 60°Brix. From 50°Brix to 60°Brix, no difference in the effective diffusivities was observed.

It was also studied the equilibrium and dynamic mass transfer properties of water and solute during osmotic dehydration of radish slices in sodium chloride (NaCl) solutions (HERMAN-LARA et al., 2013). The experiment was performed using 0.05, 0.15 and 0.25 g/g solutions at different temperatures (25, 40, 55 and 70°C) using a brine-to-vegetable mass ratio of 15:1. Using Fick's Second Law of diffusion, the water loss and solute gain curves were mathematically described and the diffusion coefficients were estimated. Effective water diffusivity was in the range of 1.85 $x10^{-9}$ to $2.74x10^{-9}$ and 2.88x 10^{-9} m^2/s for each solution concentration (HERMAN-LARA et al., 2013).

Mass transfer also happens during acidification process in vegetables and fungus. This operation is important to decrease the pH of the product in order to reduce de thermal process severity (DEROSSI et al., 2011). For instance, this process was studied in Zucchini slices and mushrooms (DEROSSI et al., 2011; DEROSSI; DE PILLI; SEVERINI, 2013) where the Peleg Model was used to study the evolution of the pH ratio as a function of time. Other studies of acidification process were performed in stalk-of-palm (GOMES et al., 2006), broccoli (MUNYAKA et al., 2009) and olives (VERGARA et al., 2013).

Regarding extraction processes, mass transfer modeling was studied during supercritical fluid extraction in different products as: red pepper extracting oleoresins (SILVA; MARTÍNEZ, 2014), apricot kernel oil extraction (ÖZKAL; YENER; BAYıNDıRLı, 2005), trout fish powder fatty acids extraction (NEI et al., 2008), olive oil extraction (HURTADO-BENAVIDES et al., 2004), biomass oil (PATEL; BANDYOPADHYAY; GANESH, 2011), etc.

1.3.1 Mass transfer phenomena during the hydration process

During hydration and rehydration processes, mass transfer (water transfer) happens in different ways depending on the composition, microstructure and cellular activity of the food. For instance, water intake can occur by diffusion, capillarity or/and convective transfer. This process is used in the hydration of food that is naturally dry and the rehydration of pre dehydrated food.

However in some food like grains, the hydration process is complex. They have different tissues such as seed coat, endosperm, cotyledon and germ that probably have different water affinity. Besides some of them can be impermeable, and others can be water entrance controller. Therefore, it is very probable that the water enters into grains following a particular pathway (LUSH; EVANS, 1980; PERISSÉ; PLANCHUELO, 2004)

Many mathematical models have been used to explain the hydration kinetics of food. For example it was used the Fick's Second Law to explain the rehydration kinetics of potato cylinders (CUNNINGHAM et al., 2008), Normalized Weibull's model for rehydration of carrots (LEE et al., 2006), Peleg's model for several grain hydration kinetics (Table 1.1) and sigmoidal models for some grain hydration kinetics too (Table 1.1). However, many mathematical models used to explain the hydration process only consider it as a diffusional process without considering the complex structure that food have.

As stated above, the hydration process usually is enhanced using higher temperatures, which can cause undesirable reactions on the composition of the food. For that reason, new technologies have to be study in order to enhance the process without damaging the product.

1.4 Uses of ultrasound to improve the food mass transfer

One of the emergent applications of ultrasound in the food industry is the increment of mass transfer. Ultrasound can affect both internal and external resistance of mass transfer (MULET et al., 2003). The high intensity of ultrasound can produce agitation in the fluid causing the reduction of external resistance (WELTI-CHANES; VELEZ-RUIZ, 2002). The ultrasound also generates pressure difference in the solid/liquid interface and it increases the water absorption ratio. Moreover, the ultrasound produces a rapid series of contractions and expansions (sponge effect) in the material in which is propagated, causing the pumping of a fluid inside it that enhances the mass transfer by reducing internal resistance (MULET et al., 2003). Besides, cavitation can cause tissue and cell disruption inside the food generating microscopic channels which reduces the internal resistance too.

All of these mechanisms of mass transfer enhancement were attributed in different process. However, they have not been demonstrated and discriminated yet. It is possible that in some food, only one or many of those mechanisms take place. For that reason, it is necessary to perform more studies in order to demonstrate them. Some studies using ultrasound technology in mass transfer unit operations are presented below.

Sonication involved a significant improvement of mass transfer processes during the convective drying since it increases effective moisture diffusivity. This increment was due to the reduction of internal resistance caused by the sponge effect and/or the cavitation that created micro channels facilitating the water liberation from the solid samples (CÁRCEL et al., 2011). The use of ultrasound in convective drying process improves its efficiency. Ultrasound effects maximize when it is applied in low temperatures and high ultrasonic power level. This fact is very interesting because it can be useful when thermo sensitive food need to be dehydrated in order to achieve better retention of functional and nutritional properties of the product (SABAREZ; GALLEGO-JUAREZ; RIERA, 2012).

The magnitude of ultrasound effect in drying depends on the air temperature, air velocity, mass charge density and acoustic energy. The air velocity is one of the most important variable involves in ultrasound assisted air drying (CÁRCEL et al., 2007; GARCIA-PEREZ et al., 2007). In addition, it was found that the air velocity increment produces the sound pressure level reduction in the drying chamber causing the insufficient available energy to affect the mass transfer process (RIERA et al., 2011). It was also demonstrated that the higher the ultrasound power is, the higher the diffusivity and the mass transfer coefficients values will be, accelerating the process (GARCIA-PEREZ et al., 2009).

For instance, the acoustic power used during strawberry and banana drying process enhances the effective diffusivity and the mass transfer coefficient reducing the process time and the energy use almost 40 %. In addition, it reduces the severity of the process, maintaining nutritional properties of heat sensitive food (AZOUBEL et al., 2010; GAMBOA-SANTOS et al., 2014).

The material structure could be an important factor in the ultrasound effect extension. For instance, the application of ultrasound in a food that is more porous than other, cause a more powerful ultrasound effect on mass transfer obtaining an almost ten times higher diffusivity (GARCIA-PEREZ et al., 2007). The mass density effect on ultrasound effectiveness for hot drying process in carrot cubes was not significant in the water diffusivity; however, it produced a reduction of mass transfer coefficient. This phenomenon could be due to disturbances in the flow of air through the drying chamber, which created preferential paths and, as a consequent, external mass transfer resistance was increased (CÁRCEL et al., 2011). When higher intensity of ultrasound is applied, the mass transfer coefficient and water diffusivity effectiveness is enhanced when mass charge density (quantity of sample) used is moderated; nevertheless, the acoustic influence on mass transfer coefficient become negligible when mass charge density is very high (CÁRCEL et al., 2012).

The ultrasound has also been studied with the osmotic dehydration process. For example, the ultrasound assisted osmotic dehydration of strawberries was studied, reducing the process time and increasing effective water diffusivity to 37 %. The micro channels formed by ultrasound were considered as the responsible of time process reduction (GARCIA-NOGUERA et al., 2010). In addition, ultrasonic treatment increased water diffusivity during osmotic dehydration of melon due to micro channels formation which offered lower resistance to water diffusion (FERNANDES; GALLÃO; RODRIGUES, 2008).

The extraction of organic compounds from plants and seeds using solvents is also significantly improved by ultrasound. The mechanic effect cause better solvent penetration in cell and enhances the mass transfer (MASON; PANIWNYK; LORIMER, 1996). This better penetration is due to the high power of ultrasound which cause cavitation of bubbles enhancing mass transfer from and to cellular interfaces (KNORR et al., 2004). For example, ultrasound assisted extraction was used for extraction of steroid alkaloids from potato peel waste (HOSSAIN et al., 2014), oil from black seed (*Nigella sativa)* (ABDULLAH; KOC, 2013), oleoresin from *Capsicum annuum* (FERNÁNDEZ-RONCO et al., 2013), antioxidants from mustard seed (*Brassica juncea*) (DUBIE et al., 2013), etc; reporting in of all them, enhancement of extraction process and reducing the severity of the process (using low temperatures and less solvent quantity).

The ultrasound technology was also used to enhance desalting process. It was studied the effect of ultrasound (750 W and 1500 W; with 40 kHz in a water bath of 71 L) on desalting kinetics and on textural and microstructural changes of cod (*Gadus morhua*) (OZUNA et al., 2014). Moisture and NaCl concentration was studied using the Fick's 2nd law, and the evolution in the swelling and hardness of cod during desalting was determined and modeled by assuming first-order kinetics. The effective diffusivity of NaCl without ultrasound application was 4.57 x 10^{-10} m^2/s, which was significantly increased with the application of ultrasound. This improvement was attributed to the sponge effect and the micro channels formation reducing internal resistance. However, it was not demonstrated. The desalting induced the tissue swelling and the decrease in sample hardness, both of which were intensified by ultrasound application. Finally, it was shown that ultrasound affected the microstructure increasing the fiber width of cod (OZUNA et al., 2014).

1.5 Enhancement of grain hydration process using ultrasound

As stated above, hydration of grains is a very important process which can be enhanced by using ultrasound technology. This technology reduces the soaking time probably by reducing the internal resistance significantly more than external resistance (CUNNINGHAM et al., 2008). This happens because of the possible changes on microstructure by cavitation (micro channel formation) or the sponge effect causing inertial flow. Unfortunately, there are few studies of grain hydration using ultrasound technology, and until now, they have demonstrated that water absorption in grains was increased when ultrasound was used. Related works are presented below.

The water absorption of chickpeas (*Cicer arietinum L.*) was significantly increased with soaking time, temperature and power of ultrasound (25 kHz - 100 W; 40 kHz - 100 W; 25k Hz - 300 W). It was demonstrated that higher frequencies of ultrasound like 40 kHz did not significantly affect the water absorption of chickpeas during soaking comparing with 20 kHz; but, the higher the ultrasound power was, the higher the hydration rate was. In addition, the combination of ultrasound technology and temperature enhanced the soaking process reducing the k_1 and k_2 value of Peleg model from 96.28 to 5.43 s % d.b.$^{-1}$ and from 7.45 x 10^{-3} to 5.94 x 10^{-3} % d.b.$^{-1}$

(YILDIRIM; ÖNER; BAYRAM, 2010). The improvement of the process was atributed to the "sponge effect". Nevertheless, without demonstrated it.

In other study, it was demonstrated that ultrasonic pre-treatment in soaking process of chickpeas (*Cicer arietinum*) could decreased the process time by up to 4h (RANJBARI et al., 2013). The authors used an ultrasonic probe (600 W of power and 24 kHz of frequency) and stated that the most probable mechanism for ultrasonic enhancement of water absorption was the collapse of cavitation bubbles near cell walls of the seed coat that caused cell disruption and the penetration of the water into cells by the ultrasonic jet. Moreover, the phenomena was explain by the probable rupture of large molecular structure that induced more water absorption points and consequently, formation of hydrogen bonding between molecular water and the structure lead to more water absorption in sample treated with ultrasound.

Moreover, the effect of ultrasound (26 W/L, 40 kHz) was studied on the hydration kinetic of sorghum grains (*Sorghum bicolor*) (PATERO; AUGUSTO, 2015). The data was fitted using the Peleg Model and it was observed that ultrasound-assisted hydration significantly reduced k_1 and k_2 values to 88% and 90% respectively from the control value. On the other hand, it was compared the process using 53°C with and without ultrasound application, and it was demonstrated that there was no significant difference between both treatments. Thus, the ultrasound is not as effective as using high temperatures for reducing the soaking time. Even though, it is very probable that it does not cause the same collateral effects than high temperatures. The enhancement of the process was attributed to the possible micro channels formation by cavitation and/or the "sponge effect".

Additionally, it was studied the effect of sonication (47 kHz and 750 W) on the hydration rate of navy beans. The hydration kinetic was described using the Fickian diffusional model, Peleg model, Weibull model and first order kinetics equation. It was demonstrated that the ultrasound enhanced the hydration process increasing the effective diffusivity for water transport from 1.63×10^{-10} m^2/s (non-sonicated process) to 2.19×10^{-10} m^2/s (sonicated process) and reducing soaking time (GHAFOOR et al., 2014). They attributed the enhancement to the micro channels formation by the acoustic cavitation that decreases the internal resistance to the mass flow. In addition, they state that the "sponge effect" also helped to improve the process. Moreover, they studied the effect of ultrasound on the pasting properties (Rapid viscosity analysis) of the navy beans flour, showing a higher peak apparent viscosity of the sonicated samples than the conventionally hydrated samples.

Finally, the ultrasound was used as pretreatment in different varieties of common beans (*Phaseolus vulgaris*) (ULLOA et al., 2015). The beans were pre-treated for 10, 20 and 30 min in an ultrasound bath (40 kHz, 0.026 W/cm^3 and 30 °C) for then being conventional hydrated. The Peleg Model and Kaptso Model were used to describe the process. The soaking time was significantly reduced, improving the hydration process when ultrasound was used. The enhancement was attributed to the micro channels formation and to the “sponge effect”. They only stated that by applying 30 min of ultrasound the behavior of the hydration change from a sigmoidal shape to a downward concave shape. In addition, the cooking time of the beans was reduces in one case up to 43 %.

1.6 Final considerations

The use of high power ultrasound for mass transfer enhancing in foods has still been slightly studied. The enhancement of the mass transfer unit operation by the ultrasound technology has been shown in many works, being attributed to different mechanisms. However, any work has still demonstrated these mechanisms, creating the need for this evaluation. Since the ultrasound technology is a promising technology, it is very important to keep studying it in order to optimize the processes and find new applications.

Relative to grains, the ultrasound effects were studied only for chickpeas, navy beans, sorghum and some varieties of common beans, obtaining successful results in reducing the process time. Thus, it is necessary to study it more using other grains with commercial importance, ultrasound conditions (power and frequency) as pre-treatment and treatment, and besides, studying the possible negative effects that, as the majority of technologies, could have. In addition, although the ultrasound has shown excellent results on the hydration process, it is necessary to perform more studies in order to demonstrate which mechanisms of enhancement take place during this process.

Due to the exposed reasons, it is very important to study firstly the hydration process phenomenon, explaining this process by giving the ways how the water is transferred to the inside of the grain. Secondly, the principal effect of ultrasound technology has to be established during this process. And finally, it has to be study the possible morphological and compositional changes when this novel technology is used. Consequently, the present work was focused on describing and explaining the effect of ultrasound on the hydration process of grains, by studying the microstructure changes, hydration kinetics and possible change on their composition properties.

1.7 Objectives

- Describe and model the hydration process of grains and study the effect of the ultrasound technology on this process.

The specific objectives were:

- Study the hydration kinetic of two grains: Andean lupin (*Lupinus mutabilis*) and Adzuki beans (*Vigna angularis*); establishing how water is transferred inside them.
- Evaluate the effect of the temperature and initial moisture content on the hydration kinetics of Andean lupin (*Lupinus mutabilis*) and Adzuki beans (*Vigna angularis*) respectively.
- Study how the mechanisms of ultrasound technology enhance the mass transfer process during the hydration of grains.
- Evaluate and model the effect of ultrasound on the hydration kinetics of corn kernels.
- Evaluate the effect of ultrasound-assisted hydration on cornstarch properties, selected as the most important industrial corn product.

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2 CORRELATION BETWEEN MORPHOLOGY, HYDRATION KINETICS AND MATHEMATICAL MODELS ON ANDEAN LUPIN (*Lupinus mutabilis* Sweet) GRAINS[1]

Abstract

This work describes the hydration kinetics of Andean lupin (*Lupinus mutabilis* Sweet) grains, correlating its morphology with mathematical models in order to explain the process. Microstructural analysis of the grains was performed using a scanning electron microscope and the hydration kinetics was determined between 23°C and 60°C. The hydration kinetics showed the sigmoidal behavior, which was fitted with two sigmoidal models. Further, this behavior was explained by the grain morphology, demonstrating that the seed coat was the cause of this behavior, related to the slow initial water intake. It was demonstrated that the water entered to the grain by diffusion through the seed coat, and by capillarity through the hilar fissure. Besides, an increase in the process temperature resulted in higher water absorption rate, smaller hydration time and higher final moisture content, enhancing the process. Each model's parameter (equilibrium moisture, water absorption rate and lag phase time) was then modeled as function of the temperature. Finally, two general models were obtained with good agreement, which can be used to predict the moisture of the grain as function of both time and temperature.

Keywords: Andean lupin; Hydration; Modeling; Morphology; Rehydration

2.1 Introduction

The Andean lupin, also called Chocho or Tarwi (NRC-US, 1989) is a legume from the Andean region, of South America, which is widely used by the local population as food and natural medicine (JACOBSEN; MUJICA, 2006). It is known by its high nutritional value, with a high content of proteins (44.3 g/100g) and unsaturated fatty acids (40.4 g/100g of omega-9, 37.1 g/100g of omega-6 and 2.9 g/100g of omega-3, with respect to the total fat content - 16.5 g/100g) (JACOBSEN; MUJICA, 2006). It is used mainly as a protein source in human and animal nutrition in various parts of the world, and its consumption has increased in recent years (GÜÉMES-VERA et al., 2008). This grain is being considered an internationally

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promising crop, especially in Peru, where its production is growing since it started to be incentivized (BRIGAS CÉSPEDES, 2014; MOHME SEMINARIO, 2014).

The hydration process in grains is a prior step to different processes such as cooking, extraction, germination and wet milling, since it prepares the grains for processing. In most cases, this stage is a batch unit operation, with a long duration (between 4 to 18 hours on average). Many studies have already been conducted about the hydration of different grains, such as adzuki beans (OLIVEIRA et al., 2013), chickpeas (GOWEN et al., 2007; IBARZ et al., 2004; YILDIRIM; ÖNER; BAYRAM, 2011), white lupin (SOLOMON, 2009), red kidney beans (ABU-GHANNAM; MCKENNA, 1997a), sesame seeds (KHAZAEI; MOHAMMADI, 2009), and so on. However, most of these works just evaluated the grain hydration using simple kinetics models, neglecting the initial lag phase that some grains have. The few studies that considered sigmoidal hydration kinetics for grains neither ensure the cause of lag phase nor explain the process morphologically giving only suppositions. Further, there is not any work in the literature studying the hydration kinetics of Andean lupin (*Lupinus mutabilis* Sweet), despite that it is an important stage because it increases the water content of the grain and enhances the alkaloids extraction in the subsequent stages (CARVAJAL-LARENAS et al., 2013).

The present work correlated the morphology, hydration behavior and mathematical models in order to explain and predict the hydration kinetics of Andean lupin (*Lupinus mutabilis* Sweet) grains.

2.2 Materials and Methods

2.2.1 Water uptake behavior

Andean lupin grains (*Lupinus mutabilis* Sweet) (9.08 ± 1.44 g/100g d.b moisture, 9.98 ± 0.64 mm length, 8.39 ± 0.41 mm width and 6.02 ± 0.35 mm thick) were purchased in a local market of Trujillo – Perú. The Andean lupin used was breed in the north Andean region of Perú (La Libertad ~3200 masl (meters above the sea level)). After harvest, the grains were stored for 2 months before being sold. The grains were selected by eliminating those that were not intact and stained. The grains were stored in a bag of low-density polyethylene (~15.6 µm thick) at average room temperature of 20 ± 2 °C and 60% RH before processing.

For microstructural analysis, samples of grains were cut using a scalpel blade in order to see the different tissues (seed coat, cotyledon, and external surface) and dehydrated using silica gel for 3 days in a closed container. Then, they were sputtered with a 30 nm gold layer. Finally, the samples were observed in a scanning electron microscope operated at an acceleration voltage of 15 kV (LEO 435 VP, Leo Electron Microscopy Ltd., Cambridge, England).

In order to establish the principal mechanism of water entrance into the grains, they were hydrated in a solution of brilliant blue 0.01 g/100mL (food grade, gently donated by SanLeon, Brazil, www.sanleon.com.br). Ten grains were normally hydrated and other ten grains were covered in the hilar fissure with a cyanoacrylate ester glue before hydration process. Images were obtained at 30, 60, 90, 120, 150, 180, 210 and 330 min of the grains previously rinsed with distilled water and superficially dried with toilet paper.

2.2.2 Modeling hydration kinetics as function of temperature

The hydration procedure was carried out in the same way as described in previous works (for example, (YILDIRIM et al., 2010)). In each replicate, 40 g of Andean lupin grains were immersed in 800 mL of distilled water (proportion of 1:20, in order to ensure the excess of water). Then, they were immersed in a water bath to control the temperature of processing (23, 30, 40, 50 and 60°C ± 1°C). At each 30 min interval, approximately 2 g of grains and 40 mL of water was taken out to maintain the grains-water ratio constant. Then, the grains were superficially dried with absorbent paper in order to determine the moisture content by oven method (ASSOCIATION OF ANALYTICAL COMMUNITIES - AOAC, 1990). The procedure was conducted until stabilization and replicated four times.

The Andean lupin hydration kinetics was modeled using appropriate mathematical functions, as described further. For that, the amount of water absorbed in grams per 100 grams of dry matter (g/100g) versus time of the hydration process was tabulated for each evaluated temperature. The data were fitted to the mathematical model with a confidence level of 95% using the Levenberg-Marquardt algorithm in Statistica 12.0 (StatSoft) software.

Then, the model parameters were evaluated and modeled as function of the temperature using appropriate mathematical functions. For them, the same procedure using the software Statistica 12.0 was used.

Finally, the goodness of the models fitting was evaluated by the coefficient of determination (R^2) of the regression value, the root-mean-square deviation values (RMSD, eq. (2.1)), the normalized RMSD (NRMSD, eq. (2.2)) and by plotting the moisture values obtained by the model (M_{model}) as a function of the experimental values ($M_{experimental}$). The fitting of those data to a linear function (eq. 2.3) results in three parameters that can be used to evaluate the description of the experimental values by the model, i.e. the linear slope (a; that must be as close as possible to one), the intercept (b; that must be as close as possible to zero) and the coefficient of determination (R^2; that must be as close as possible to one). It is a simple and efficient approach to evaluating the model fit.

$$RMSD = \sqrt{\frac{\sum_{i=1}^{n}(M_{experimental} - M_{model})^2}{n}} \tag{2.1}$$

$$NRMSD = 100 \cdot \frac{RMSD}{(M_{experimental})_{maximun} - (M_{experimental})_{minimun}} \tag{2.2}$$

$$M_{model} = a \cdot M_{experimental} + b \tag{2.3}$$

2.3 Results and Discussion

2.3.1 Andean lupin hydration kinetics

The effect of temperature on the moisture content of Andean lupin grains is shown in Figure 2.1. The moisture increased with the duration of soaking and a lag phase at the first part of the curve can be clearly seen, where the water uptake rate was low at all evaluated temperatures. Thus, the grain hydration can be described by a sigmoidal behavior, with an initial lag phase followed by a higher absorption rate phase and, finally, by a stationary phase.

This behavior is similar to different grains such as adzuki beans (OLIVEIRA et al., 2013), cowpeas (KAPTSO et al., 2008; SEFA-DEDEH; STANLEY, 1979), lima beans (PIERGIOVANNI et al., 2012) and badda bianco and badda nero beans (PIERGIOVANNI; ANGELA ROSA, 2011), although most of the cited works have not appropriately described this behavior. This behavior is attributed, in the literature (KAPTSO et al., 2008; OLIVEIRA et al., 2013), to the seed coat resistance to the mass transfer phenomenon (water flow), although it was still not demonstrated. In addition, most of the grain hydration behavior were described in the literature by simple downward concave shape curves, mostly described by the Peleg Model (PELEG, 1988). In that behavior, the lag phase does not exist, probably because the seed coat exerts a very small resistance to the water flow (ABU-GHANNAM, 1998; ABU-GHANNAM; MCKENNA, 1997a; ABU-GHANNAM; MCKENNA, 1997b; JIDEANI; MPOTOKWANA, 2009; PIERGIOVANNI, ANGELA ROSA, 2011; SOLOMON, 2009). It is interesting to observe that there is a work in the literature where the hydration kinetics of roasted lupin (*Lupinus albus*) was fitted to the Peleg Model despite that the data showed sigmoidal behavior (SOLOMON, 2009).

Therefore, the mathematical modeling of the Andean lupin grains hydration process was conducted using the two sigmoidal functions described in the literature: eq. (2.4) (KAPTSO et al., 2008) and eq. (2.5) (IBARZ; AUGUSTO, 2014); where M_t is the sample moisture content at each time t, τ describes the inflection point, being thus related to the lag phase, k_K is the water absorption rate kinetics parameter, M_{eq} is the equilibrium moisture content (maximum absorbed moisture), M_o is the initial moisture content and k_{IA} is a kinetics parameter related to the lag phase and water absorption rate. The goodness of both models fitting was good, describing well the experimental values and obtaining R^2 always higher than 0.96 for each replicate. It can also be clearly seen in Figure 2.1, where the curves represent the values obtained by the models.

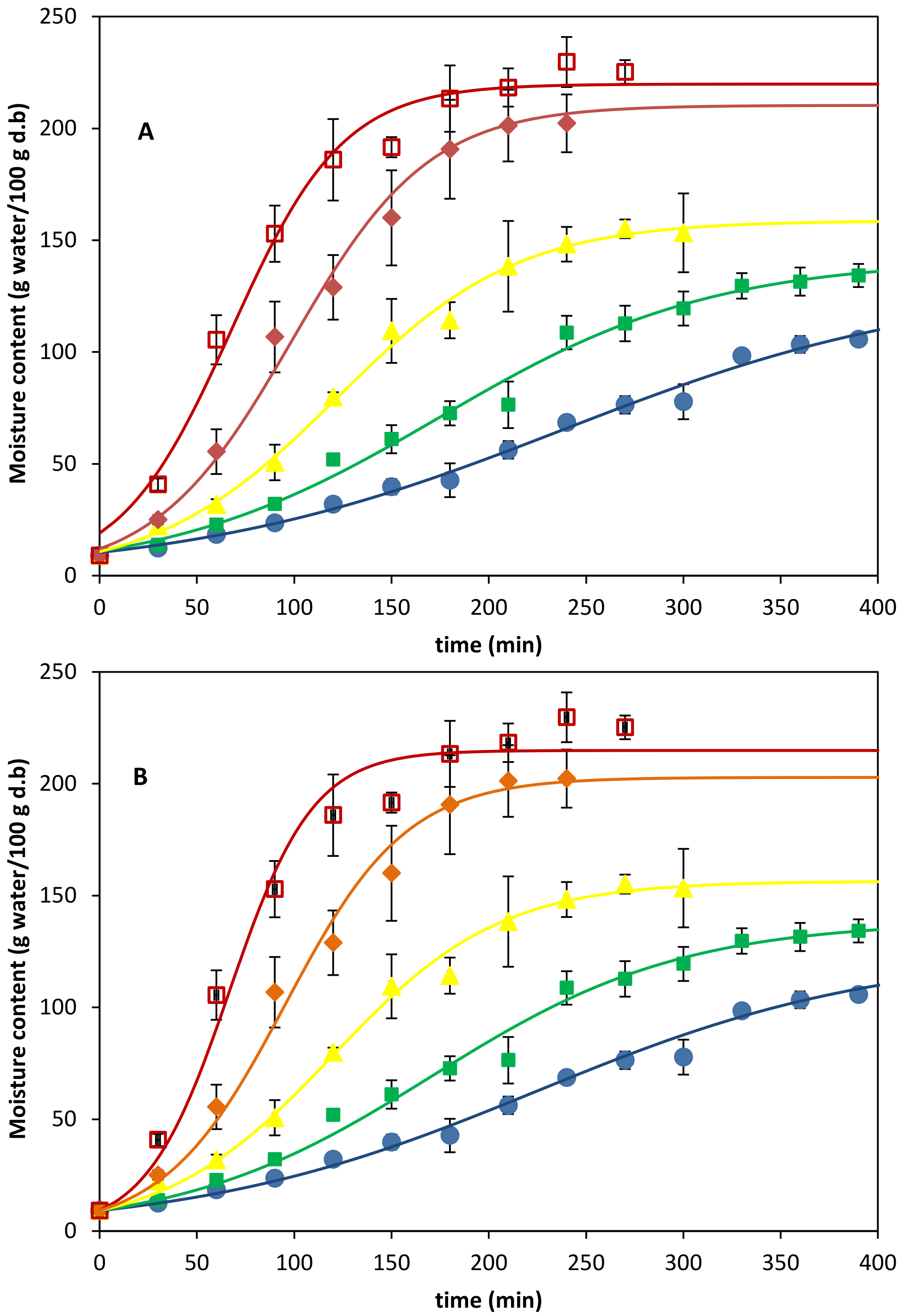

Figure 2.1 – Water uptake behavior in Andean lupin grains at different temperatures (T(°C): ● 23, ■ 30, ▲ 40, ♦ 50 and □ 60). The dots are the experimental values; the vertical bars the standard deviation and the curves are the sigmoidal model (eq. (2.4) and eq. (2.5)) (A. Kaptso et al. model and B. Ibarz-Augusto model)

As both hydration models described well the Andean lupin behavior, the following evaluation was carried out using them.

$$M_t = \frac{M_{eq}}{1+exp[-k_K.(t-\tau)]} \tag{2.4}$$

$$M_t = \frac{M_{eq}}{1+\frac{M_{eq}-M_O}{Mo}\exp(-k_{IA}\cdot M_{eq}\cdot t)} \tag{2.5}$$

2.3.2 Explanation of Andean lupin water intake behavior

Although many works have presented the hydration processes of different products in the literature, the exact mechanism of mass transfer during hydration is still not completely understood. For example, there are just a few works in the literature partially describing the sigmoidal behavior during hydration (KAPTSO et al., 2008; OLIVEIRA et al., 2013). Many others do not describe the sigmoidal behavior, even though the presented data clearly showed it (PIERGIOVANNI; ANGELA ROSA, 2011; SOLOMON, 2009). In consequent, the reason for the sigmoidal behavior has not been proven in the literature yet.

The water absorption during soaking of Andean lupin grains with and without its seed coat is presented in Figure 2.2. It can be observed that seed coat exerts a high resistance to the hydration process not only by reducing the water absorption rate, but also by changing the shape of the curve. While the whole grains show a sigmoidal behavior during hydration, the uncoated grains clearly show a downward concave shape behavior (as described by the Peleg Model – (PELEG, 1988)). Consequently, it clearly demonstrates that the seed coat is the main cause of the sigmoidal shape hydration kinetics, and confirms the previous statements of Kaptso et al. (2008) and Oliveira et al. (2013).

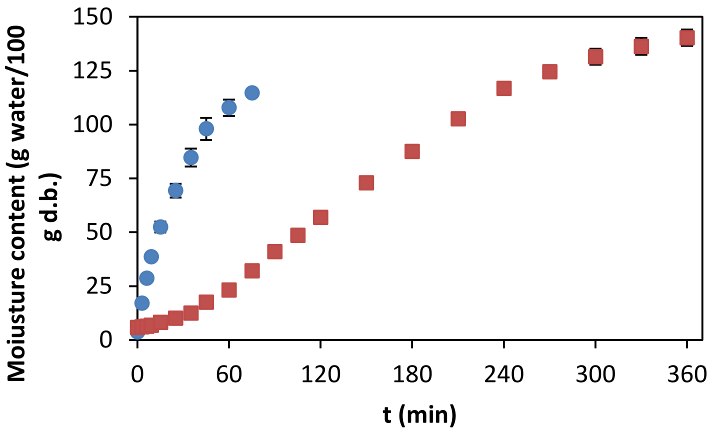

Figure 2.2 – Hydration kinetics of Andean lupin with seed coat (■) and without seed coat (●) at 30°C. The dots are the experimental values; the vertical bars the standard deviation

The external morphology of the Andean lupin grain (Figure 2.3) has a structure called hilum and hilar fissure where it was demonstrated as the principal water entrance into the grain. Figure 2.4 shows the water and colorant solution pathway through the grain in two conditions (normal grain and hilar fissure covered grain). In the first condition, it was noticed that colorant solution entered first by the hilar fissure routed by a structure (directional structure or radicle pocket (Figure 2.5) which ensured the radicle hydration. Then, the water filled the seed coat-cotyledon space for later distributing the water into the cotyledon in a homogeneous way. It can be ensured that water also get into the grain through the seed coat since the second condition helped to confirm that. When the hilar fissure was covered, the grain hydrated anyway in the colorant solution; however, the colorant did not enter to the grain, concluding that water enters to the grain by diffusion through the seed coat while by capillarity through the hilar fissure. It should be mentioned that it is very probable that water enters by hilum fissure more quickly than by the seed coat. The water pathway in a non-covered grain was similarly described by Perissé and Planchuelo (2004) in *Lupinus Albus* and *Lupinus angustifolius*. Nevertheless, they concluded that the seed coat might participate in the grain hydration after they completely hydrate from inside and that it does not have participation in the beginning of the process. It could be possible in some grains, depending on seed coat anatomy and composition, but in Andean lupin it does not happens. Besides, the hilar fissure is considered as a water entrance regulator which opening depends on the relative humidity (LUSH; EVANS, 1980), thus, it permits the water entrance during soaking process.

The seed coat's surface is covered by cuticle compound by wax that gives impermeability to different plant tissues (GRAVEN et al., 1997). In the Figure 2.5-A, it is shown that the surface of seed coat of Andean lupin is apparently not porous. Consequently, the water intake by capillary flow should be very small or negligible, being preferably transferred by diffusion to the inner tissues.

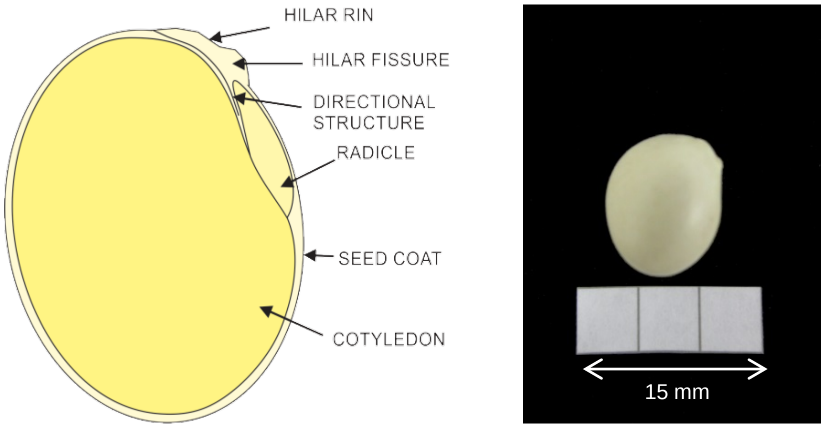

Figure 2.3 – Morphology of Andean lupin (*Lupinus mutabilis* Sweet)

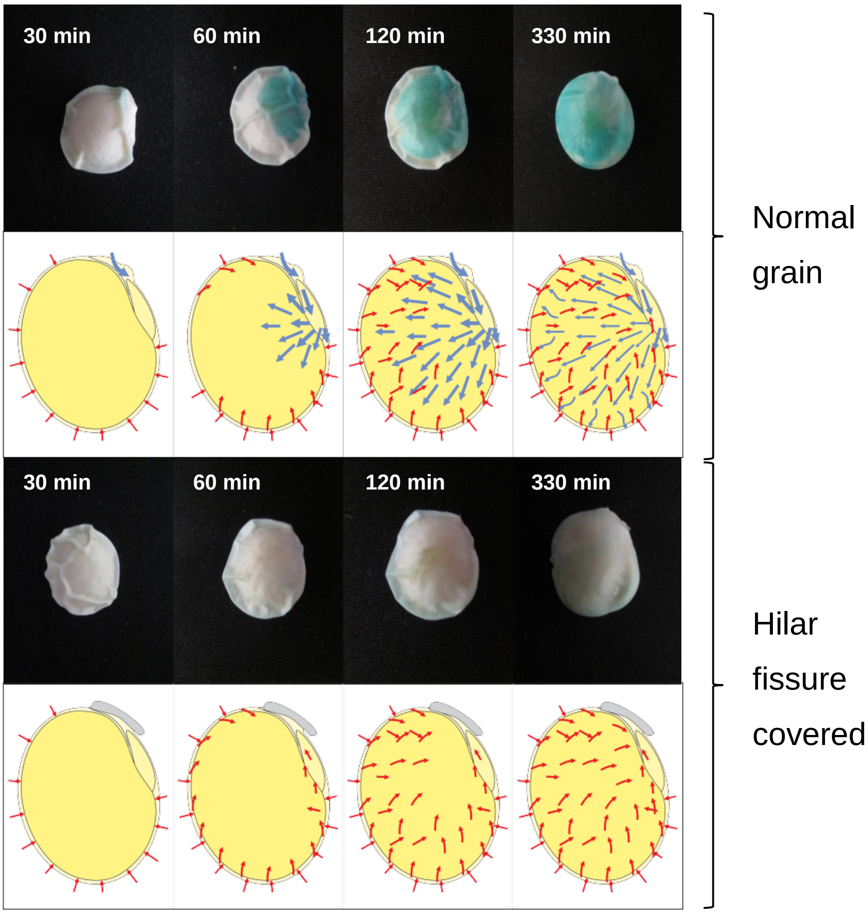

Figure 2.4 – Water intake during time in Andean lupin (*Lupinus Mutabilis* Sweet). Blue arrows indicate the entrance of colorant solution (capillarity). Red arrows indicate water entrance without colorant (diffusivity)

The Andean lupin's seed coat has three principal cells layers, which can be seen by a transversal cut (Figure 2.5-B).

The external layer is formed by macroescrereids cells (palisade tissue). These cells are died and, in *phabaceae* family, they can have different kind of hydrophobic substance like lignin polysaccharides, pectin, calose, quinones, suberin, cutin and phenols (BEWLEY; BLACK; HALMER, 2006; CASTILLO; GUENNI, 2001). This layer also gives the impermeability to the Andean lupin grain. It can be the main reason for the resistance to the water intake and, it is very probable that water transferring through that is by diffusion, according to its microstructure.

The second layer is formed by osteoesclereids cells that have bone shape and a wide intercellular space in which water can cross principally by capillarity.

The third layer is a sclerified parenchyma formed by many layers of died crushed cells. In this layer, water is probably transferred by diffusion to enter to the dyed cell, by capillarity to cross the cell interspace and by diffusion again to leave the cell to enter to the next layer of parenchyma.

Once the seed coat-cotyledon space is practically filled of water, the water absorption rate increased and the lag phase finished. In this stage, water had to cross the cotyledon of the grain. According to Figure 2.5-C, between the seed coat and cotyledon, there is a layer known, as endosperm remains formed by aleurone cells and parenchyma. This part is compound by residual nutrients (lipids and proteins) that were given to the principal reserve tissue (cotyledon) (SHEWRY; CASEY, 1999). Cotyledon and endosperm's remains have intercellular spaces that can measure approximately 9 μm as maximum (Figure 2.5-D) where water can be transferred by capillarity. Besides, the principal component of these cells is proteins (~44.3 g/100g (JACOBSEN; MUJICA, 2006)) which can give polarity to the media and hold water in their structure. For that reason, the water intake in this part of the grain was quickly until raising the equilibrium moisture.

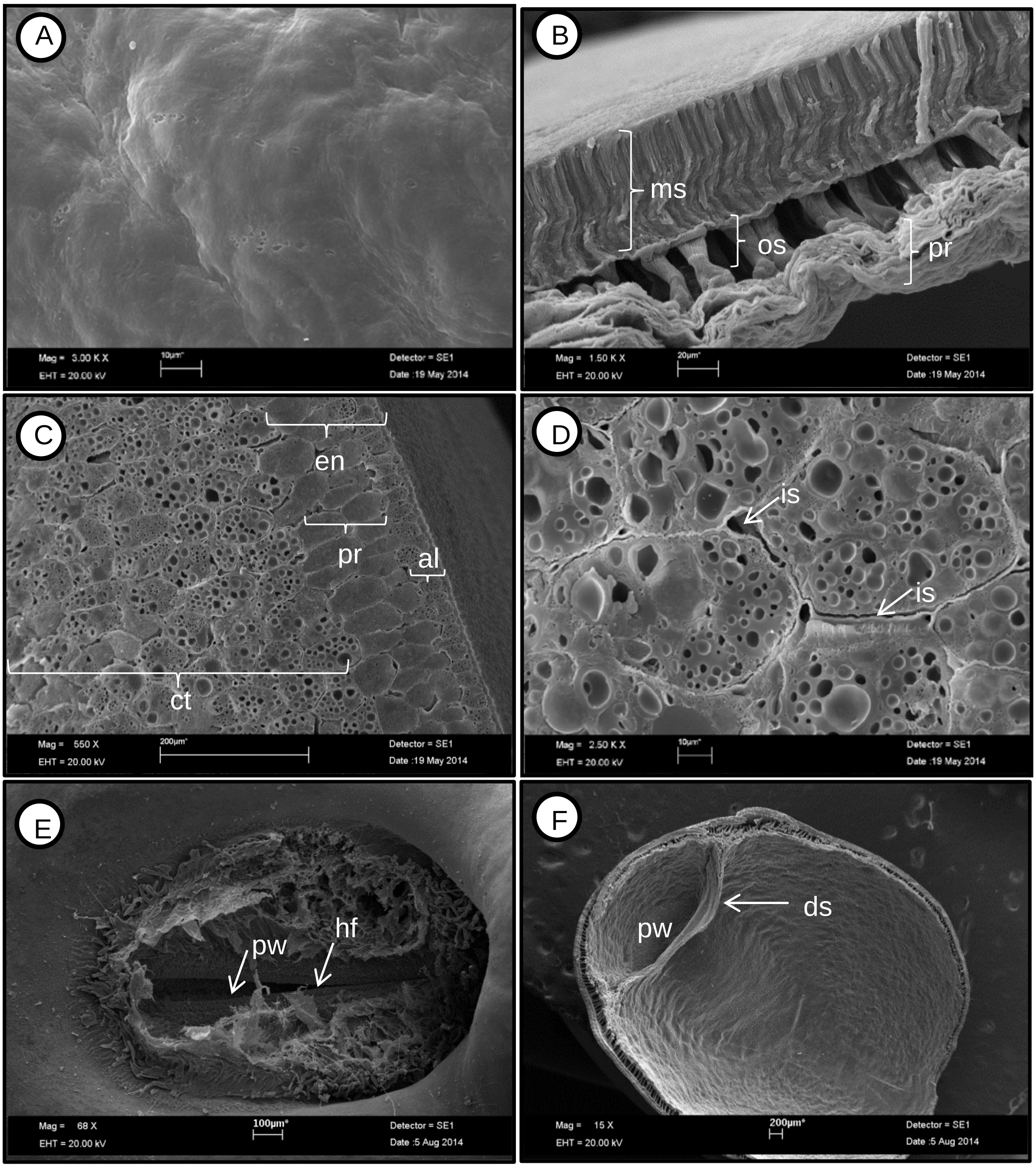

Figure 2.5 – Microphotography SEM of lupin's main microstructure (*Lupinus mutabilis* Sweet). A. External surface of seed coat. B. Transversal cut of seed coat: ms. Macrosclereids, os. Osteosclereids, pr. Parenchyma; C and D. Transversal cut of Cotyledon: en. Endosperm remains, al. Aleurone cells, pr. Parenchyma, ct. Cotyledon, is. Intracellular spaces; E. Hilum: pw. Principal water entrance, hl. Hilar fissure; F. Hilum view from the inside; ds. Directional structure, pw. Principal water entrance

One of the main functions of seed coats is to regulate the water intake rate (BORGUETTI, 2008). Entire lupin grain approximately needs six hours to reach the maximum moisture; in contrast, lupin's cotyledon only needs a little over an hour to reach the maximum moisture content. Moreover, the seed coat helped lupin grains to maintain more water inside itself. *L. Mutabilis* Sweet is the specie with less amount of seed coat of all species of *Lupinus* (~12.7 g/100g of the grain weight as mean) (CLEMENTS et al., 2005). Even so, it has more than other legumes like soybean and red kidney bean (~7 g/100g and ~8 g/100g, respectively) (LUSH; EVANS, 1980). In addition, the water absorption is avoided by macroesclereids cells in palisade tissue presented on the seed coat of Leguminosae family (BORGUETTI, 2008) and regulated by the hilar fissure in the hilum.

Therefore, it can be concluded that the seed coat, due to both its structure and composition, is the main reason for the sigmoidal behavior during the hydration of Andean lupin grains.

2.3.3 Andean lupin hydration kinetics modeling as function of temperature

The temperature of the experiments was between 23°C to 60°C, because lower temperatures imply additional cost in refrigeration (refrigeration costs are higher than heating) and a longer process (which is highly undesirable) and higher temperatures can cause undesirable changes on this grain like proteins denaturation. It is well known that the increase in process temperature improves the hydration process of grains, highlighting the importance for modeling the effect of temperature on the hydration parameters of Andean lupin. Consequently, the sigmoidal model parameters were modeled as function of temperature. Figure 2.6, Figure 2.7, Figure 2.8 and Figure 2.9 show the effect of temperature on the model parameters M_{eq} (both models), k_k, τ and k_i respectively.

Regarding the equilibrium moisture content (Meq), in both studied models, the higher the soaking water temperature, the higher was the equilibrium moisture. This behavior was similar to most of the studied grains, such as sesame seeds (KHAZAEI; MOHAMMADI, 2009), botswana bambara bean (JIDEANI; MPOTOKWANA, 2009), wheat (MASKAN, 2001), roasted white lupin (SOLOMON, 2009) and sorghum (KASHIRI et al., 2010), being also highly desirable. The increment of temperature causes, in the majority of cases, changes on cell wall structure, composition and compactness of the grain, so grains can hold more water in its structure (SABAPATHY, 2005; SIDDIQ; BUTT; SULTAN, 2011). Further, at higher temperatures, the solutes solubility is higher and the product and its pores are expanded, allowing a higher water holding. The equilibrium moisture content was then modeled as function of the temperature. Due to its behavior, it was modeled using linear equations (eq. (2.6) and eq. (2.7)) with a R^2 of 0.945 for Katpso et al. model and 0.963 for Ibarz-Augusto model (Figure 2.6).

$$M_{eq}(T) = 2.6461 \cdot T - 657.6 \tag{2.6}$$

$$M_{eq}(T) = 2.6125 \cdot T - 651.8 \tag{2.7}$$

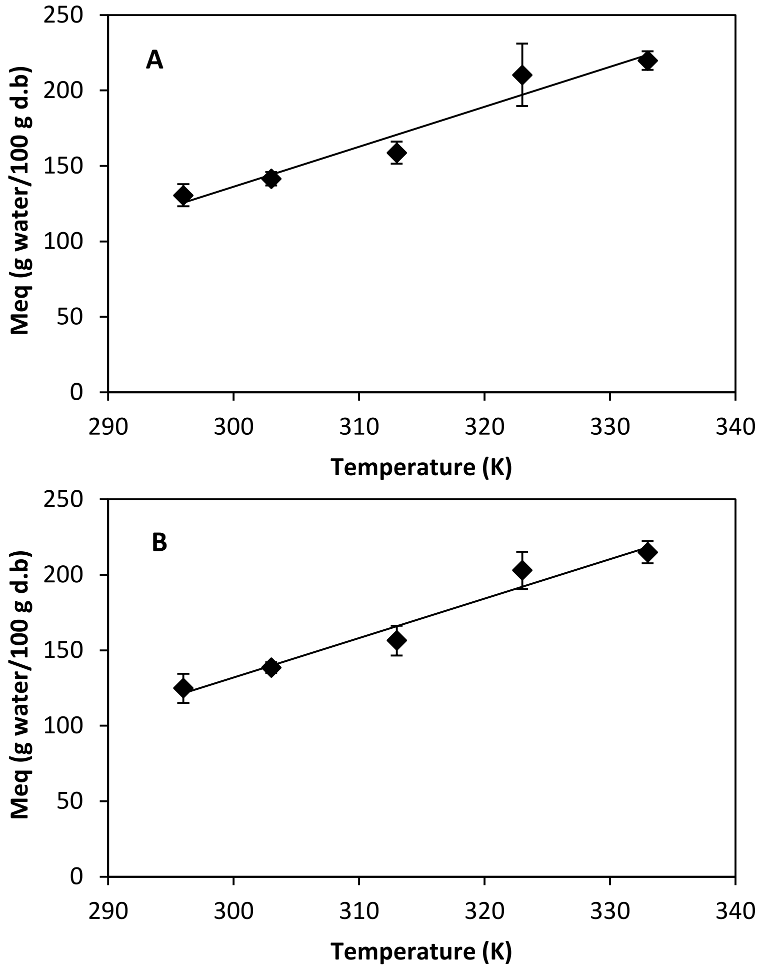

Figure 2.6 – Effect of temperature on the equilibrium moisture content (Meq). The dots are the experimental values; the vertical bars the standard deviation and the curve is the linear model (eq. (2.3) and eq. (2.4)) (A. Kaptso et al. model and B. Ibarz-Augusto model)

The hydration rate increased exponentially in relation to the increased temperature. It means that the water flow through the product is expected to be faster at higher temperatures due to the lower fluid viscosity and higher grain pores dimension (especially in cotyledon), facilitating both diffusion and capillary flow mass transfer phenomena. Further, structural changes on the cells and tissues can enhance the water absorption rate, such as the partial degradation of pectin and solubility of cell wall polysaccharides (OLIVEIRA et al., 2013; SIDDIQ et al., 2011). It explains the observed behavior, which was similar to other grains, such as adzuki beans (OLIVEIRA et al., 2013), cowpea (KAPTSO et al., 2008), rice (BELLO et al., 2004), chickpeas (GOWEN et al., 2007), bambara beans (JIDEANI; MPOTOKWANA, 2009) and roasted white lupin (SOLOMON, 2009). The hydration rate is represented by the parameter k_K on the Kaptso et al. model, and k_{IA} on the Ibarz-Augusto model. Therefore, both parameters were evaluated by the Arrhenius equation, a widely used model to describe the effect of temperature on different physic-chemical properties. It is composed by an exponential function, where the activation energy (Ea) describes the property variation with temperature (T in K), and where R is the universal constant of the ideal gas ($R = 8.314\ J \cdot mol^{-1} \cdot K^{-1}$).

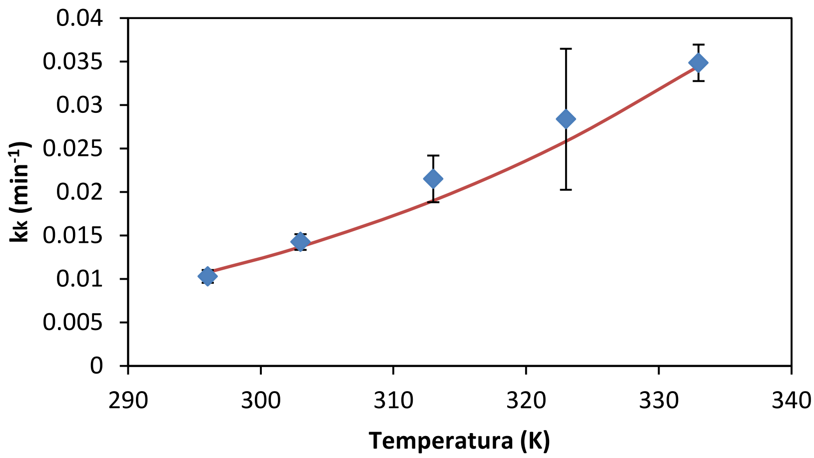

Figure 2.7 – Effect of temperature on the water absorption rate of the Kaptso et al. model ($\boldsymbol{k_k}$). The dots are the experimental values; the vertical bars the standard deviation and the curve is the Arrhenius Model (eq. 2.8).

The kinetics parameter k_K (water absorption rate) was successfully modeled using the Arrhenius model (eq. 2.8) with a R^2 of 0.99 (Figure 2.7).

$$k_K(T) = 381.668 \cdot e^{\frac{-25781.7}{R \cdot T}} \quad (2.8)$$

In addition, the parameter k_{IA} of Ibarz-Augusto model also exponentially increases with the increment of the temperature (Figure 2.8). This parameter is related to both the lag phase of the curve and the water absorption rate, as, for sigmoidal behavior grains, as higher the hydration rate, lower is the lag phase (IBARZ; AUGUSTO). As the temperature increases, the water absorption rate increases and the lag phase become shorter, reducing the hydration time. Since the seed coat-cotyledon space has to be first filled with water, the decrease of water viscosity can cause the rapid distribution of it reducing the lag phase. Further, the thermal dilatation can also increase the seed coat-cotyledon space. Besides, the higher temperatures can cause the faster opening of the hilar fissure, entering more water in the beginning of the process and reducing the lag time. The Arrhenius equation was also used to explain this behavior (R^2 = 0.96, (eq. 2.9)), with high agreement.

$$k_{IA}(T) = 0.1485 \cdot e^{\frac{-18144.5}{R \cdot T}} \quad (2.9)$$

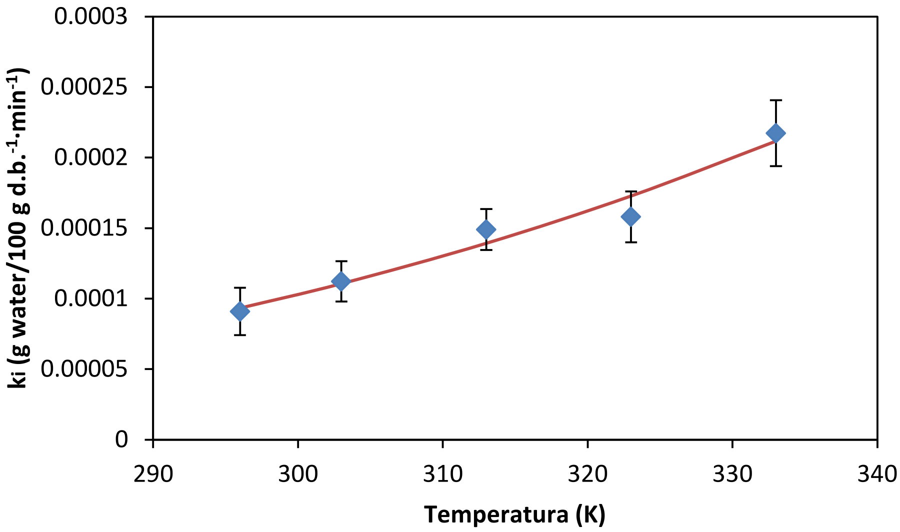

Figure 2.8 – Effect of temperature on the constant $\boldsymbol{k_I}$ of the Ibarz-Augusto model. The dots are the experimental values; the vertical bars the standard deviation and the curve is the Arrhenius Model (eq. 2.10)

Furthermore, the value of the parameter τ on Kaptso et al. model, which is related to the lag phase length (as it is the time of the inflexion point), exponentially decreases with the increment of temperature (Figure 2.9). It means that at higher temperatures, the lag phase decreases, although the hydration still fits the sigmoidal behavior. The τ reduction can be related to the same explanation of k_K behavior. As the temperature is increased, the seed coat-cotyledon spaces is faster filled with water, reducing the value of τ. The Arrhenius equation was successfully used to explain this behavior ($R^2 = 0.99$, eq (10)). Similarly, other authors have observed the same behavior for adzuki and cowpea beans (KAPTSO et al., 2008; OLIVEIRA et al., 2013).

$$\tau(T) = 0.003099 \cdot e^{\frac{27641.1}{R \cdot T}} \tag{2.10}$$

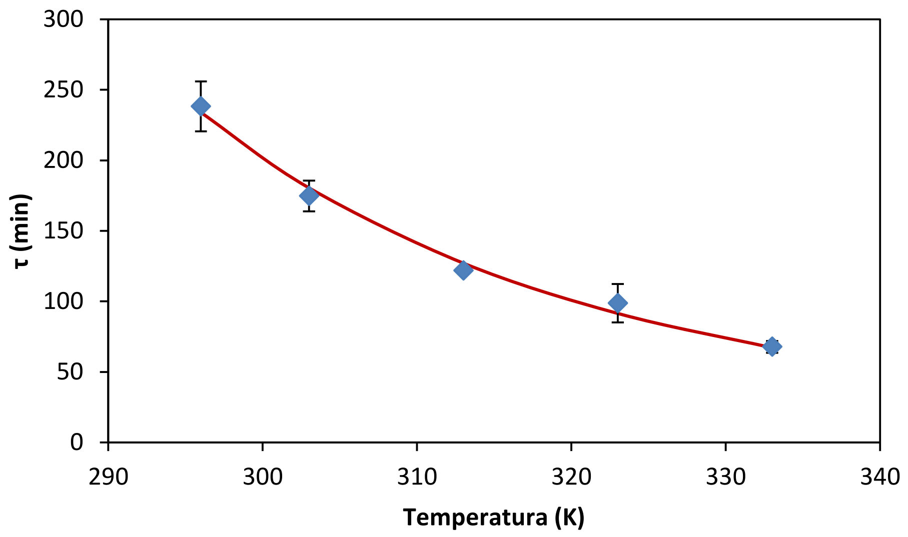

Figure 2.9 – Effect of temperature on the function inflection point in the Kaptso et al. model ($\boldsymbol{\tau}$). The dots are the experimental values; the vertical bars the standard deviation and the curve is the Arrhenius Model (eq. (2.9))

Finally, all the obtained parameters could be combined in only one equation, for each model, describing the Andean lupin grain moisture content as a function of both time (min) and temperature ($296 \leq T(K) \leq 333$) of soaking. These models are shown in eq. (2.11) and eq. (2.12) for Kaptso et al. and Ibarz-Augusto models, respectively, with $R^2 > 0.98$. Besides, the models were plotted in a 3D surface, being shown on Figure 2.10. Both surfaces describe that the higher the soaking temperature is, the faster the water uptake is which involves a shorter lag phase time, a more inclined slope (water absorption rate) and a higher equilibrium absorbed water. Further, it can clearly be seen that even at the higher temperatures, the grain hydration behavior is still sigmoidal.

$$M(t,T) = \frac{2.6461 \cdot T - 657.6}{1+\exp((-381.668 \cdot \exp\left(-\frac{3101}{T}\right) \cdot (t - 0.003099 \cdot \exp\left(\frac{3324.64}{T}\right))} \tag{2.11}$$

$$M(t,T) = \frac{2.6125 \cdot T - 651.8}{1+\frac{2.6125 \cdot T - 651.8}{9.0771} \cdot \exp(-0.1485 \cdot \exp\left(-\frac{2182.4}{T}\right) \cdot (2.6125 \cdot T - 651.79) \cdot t} \tag{2.12}$$

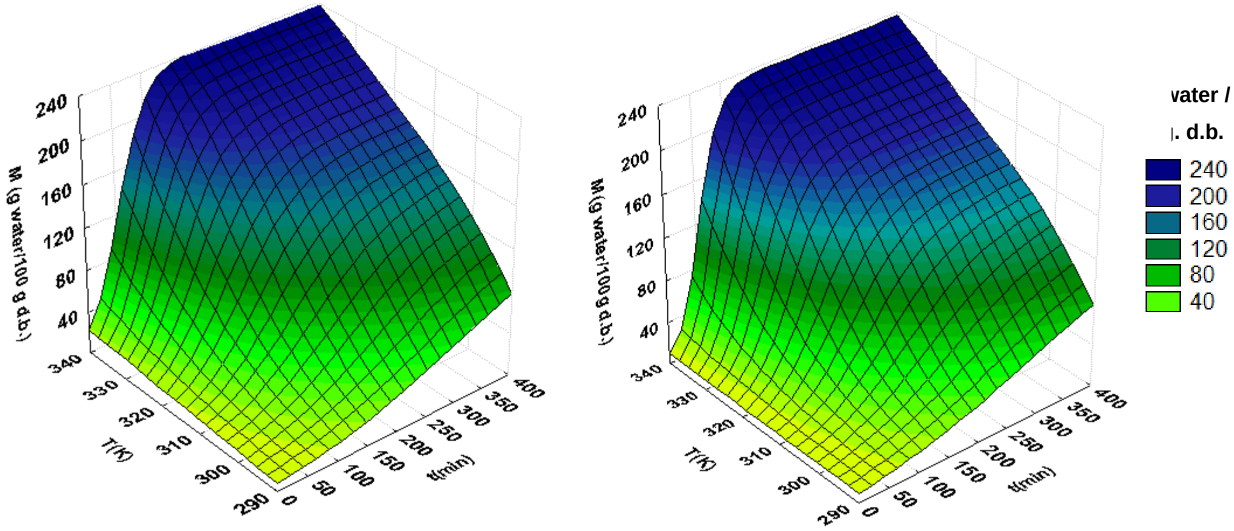

Figure 2.10 – Generated surface describing the Andean lupin grains moisture content as function of the temperature and time of soaking (A) Kapto et al. model (eq. (2.11)), (B) Ibarz-Augusto Model (eq. (2.12))

The values obtained by the models (eq. (2.11) and eq. (2.12)) were then plotted with the experimental ones in order to assure the goodness of it. It was obtained a well-fitted linear equation (R^2 = 0.991, eq. (2.13) for Kaptso et al.model and R^2 = 0.989, eq. (2.14) for Ibarz-Augusto model) that demonstrated they can be successfully used to predict the moisture of Andean lupin. Therefore, the parameter a and b from eq. (2.4) are very close to one and zero, respectively, in eq. (2.13) and eq. (2.14). The Ibarz-Augusto model fitted better the experimental data according to these parameters (Table 2.1). In addition, the root-mean-square deviation (RMSD) and the normalized RMSD (NRMSD) values were calculates (Table 2.1). Once again, the Ibarz-Augusto model obtained the lowest values, which implied less error and better adjustment.

$$M_{model} = 0.9877 \cdot M_{experimental} + 1.9511 \qquad (2.13)$$

$$M_{model} = 1.0109 \cdot M_{experimental} + 0.9083 \qquad (2.14)$$

The obtained results contributed to describe the soaking process in grains by correlating the morphology of the grain with the hydration kinetics behavior and by using new kind of models that could better explain the behavior of different grains. Consequently, the present work contributes with the process-structure-function relationships studies.

Table 2.1 – Parameter to evaluate the goodness of the models fitting

Evaluation parameter		**Hydration model: M = f(t, T)**	
		Kaptso et al. (eq. (2.11))	Ibarz-Augusto (eq. (2.12))
R^2	eq. (3)	0.991	0.989
A	eq. (3)	0.99	1.01
B	eq. (3)	1.95	0.91
RMSD	eq. (1)	5.97	0.953
NRMSD	eq. (2)	2.706	0.432

2.4. Conclusions

The Andean lupin grains (*Lupinus mutabilis* Sweet) hydration follows a sigmoidal behavior, which was proven to be due to the seed coat and the first distribution of water into it. Since seed coat has the function of controlling water intake in the grain by waterproofing, it reduces the water absorption rate almost six times and allows higher water holding capacity. Besides, it was demonstrated that the water entrance into the grain is carried out both by capillarity through the hilar fissure, and diffusion through the seed coat. Further, as soaking water temperature increased, the water intake rate also increased, reducing the process time and increasing the equilibrium moisture content. The grains hydration was successfully described by two sigmoidal models (Kaptso et al. and Ibarz-Augusto), whose parameters were modeled as function of the temperature.

Acknowledgements

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3 FROM THE SIGMOIDAL TO THE DOWNWARD CONCAVE SHAPE BEHAVIOR DURING THE HYDRATION OF GRAINS: EFFECT OF THE INITIAL MOISTURE CONTENT ON ADZUKI BEANS (*Vigna angularis*)[1]

Abstract

This work studied the change of the hydration behavior of Adzuki beans (*Vigna angularis*) as a function of their initial moisture content. By studying the hydration kinetics at different initial moisture contents, it was demonstrated that the hydration behavior of this grain changes from the sigmoidal to the downward concave shape (DCS) when the initial moisture content is above ~20 % d.b. This change happens when the moisture content passes from zone II to zone III of the grain's adsorption isotherm. This was attributed to the transition from the glassy state to the rubbery state, especially the in seed coat components. The seed coat is impermeable when the moisture content of the grain is low, so the water ingress is only by way of the hilum. However, when the seed coat is above ~20 % d.b. the water enters not only via the hilum, but also by way of the seed coat. The hydration behavior of the grain was modeled using a sigmoidal mathematical model, whose parameters were evaluated as a function of the initial moisture content. The water absorption rate parameter demonstrated a sigmoidal increasing behavior. The time to reach the inflexion point of the curve, related to the lag phase, showed an exponential decay. The equilibrium moisture content was not affected. Finally, a general model, which was able to predict the moisture content as a function of the initial moisture content of the grain and the process time, was obtained.

Keywords: Hydration; Modeling; Adzuki beans; Rehydration

3.1 Introduction

The grain soaking process is an important step during industrialization since it is one of the first steps in many grain processes. For instance, this process is performed to reduce cooking time, to facilitate starch gelatinization and protein denaturation, and to facilitate the extraction of some components (starch, protein, phenols, tannins, etc.) (ABU-GHANNAM, 1998; DESHPANDE; BAL, 2001; SIDDIQ et al., 2011). Moreover, this process is used before germination (SINGH; ECKHOFF, 1996) and fermentation (EGOUNLETY; AWORH, 2003).

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The water uptake of the grains can show two forms of behavior, which are differentiated by the mass transfer rate at the beginning of the process (Figure 3.1). In the downward concave shape (DCS) behavior, the water influx rate is a maximum at the beginning of the process (at $t \to 0$), falling to zero after enough time has elapsed (at $t \to \infty$) to reach the product equilibrium moisture content (M_{eq}). Among many models, the Peleg Model (PELEG, 1988) is the most widely used equation to describe this behavior. The sigmoidal behavior is described by an initial lag phase, i.e., an initial phase with a low water uptake rate. In this case, the water influx rate firstly increases, until an inflexion point (at $t = t_{inflexion}$) is reached. After that, the rate decreases to zero (at $t \to \infty$), when the product reaches its equilibrium moisture content (M_{eq}). This behavior can be described by the Kaptso et al. model (KAPTSO et al., 2008) or by the Ibarz-Augusto model (IBARZ; AUGUSTO, 2015).

The sigmoidal behavior is of higher interest, since it is the lag phase that slows the process. All the grains that presented this behavior are from *Leguminosae* or *Fabacea* family, like cowpea (KAPTSO et al., 2008), common bean (PIERGIOVANNI, ANGELA ROSA, 2011), lima bean (PIERGIOVANNI, ANGELA R et al., 2012), adzuki beans (OLIVEIRA et al., 2013) and andean lupin beans (MIANO; GARCÍA; AUGUSTO, 2015). In order to increase the knowledge of the sigmoidal behavior, the objective of this study was to evaluate the effect of the initial moisture content on the hydration kinetics of Adzuki beans (*Vigna angularis*), a grain with clear sigmoidal hydration kinetics. Therefore, this work combined and related the grain structure, initial moisture content and hydration rates, in order to understand and describe the phenomena.

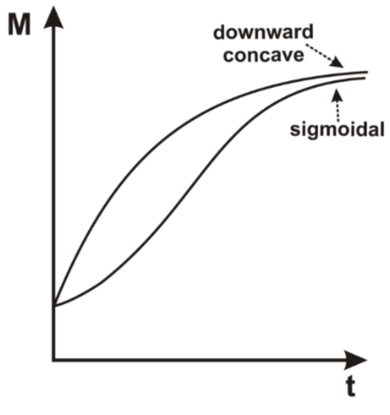

Figure 3.1 – General behaviour of grains during hydration: downward concave (DCS) and sigmoidal shapes

3.2 Material and Methods

3.2.1 Sample preparation

The Adzuki beans were obtained at a local market of Piracicaba (SP, Brazil), with a moisture content of 14.96±0.16 % d.b. (g water / 100 g of dry matter). In order to prepare samples with a higher initial moisture content (19.66, 22.44, 26.76, 29.25 and 75.00 % d.b.) the grains were hydrated for a specific time at 32.5 °C using the mathematical model obtained in a previous study (OLIVEIRA et al., 2013). Then, these grains were put into sealed containers for a week at 5 ºC in order to homogenize the moisture into the grains. The lower initial moisture content sample (4.23 % d.b.) was prepared by placing the grains in a desiccator with silica gel for 2 weeks until obtaining the required moisture content. The initial moisture content of the samples was then obtained by a mass balance using the moisture content of the original sample.

3.2.2 Hydration process and mathematical modeling

For the hydration process, 10 g of pre-selected grains were soaked in 250 mL of distilled water at 35°C using a water bath at different conditions of initial moisture content (M_0). During the hydration process, the samples were periodically drained, superficially dried and its moisture content was obtained by a mass balance. The sampling was carried out each 20 min for the first hour and each 30 minutes for the later hours, until a constant mass was obtained. The hydration process was performed in triplicate.

The Adzuki bean hydration kinetics was modeled using the Kaptso et al. Model (eq. (3.1); KAPTSO et al., 2008) and the Peleg Model (eq. (3.2); (PELEG, 1988) depending on the hydration behavior (sigmoidal or DCS behavior) (Figure 3.1). For that purpose, the dry basis moisture content of the grains (M % d.b.) versus hydration time (min) was tabulated for each initial moisture. The data were fitted to the mathematical model with a confidence level of 95% using the Levenberg-Marquardt algorithm in Statistica 12.0 (StatSoft, USA) software.

$$M_t = \frac{M_{eq}}{1+exp[-k_K.(t-\tau)]} \quad (3.1)$$

$$M_t = M_o + \frac{t}{k_1 + k_2 . t} \tag{3.2}$$

Where M_t is the sample moisture content (% d.b.) at each time t and M_{eq} is the equilibrium moisture content. In the Kaptso et al. Model (eq. (3.1)) τ describes necessary time to reach the inflection point of the curve, being thus related to the lag phase, k_k is the water absorption rate kinetics parameter. In the Peleg Model (eq. (3.2)), M_o is the initial moisture content, k_1 is a parameter relate to the water absorption rate and k_2 is a parameter related to the equilibrium moisture content.

Finally, the goodness of fit of the models was evaluated by the R^2 regression value, the root-mean-square deviation values (RMSD, eq. (3.3)), the normalized RMSD (NRMSD, eq. (3.4)) and by plotting the moisture content values obtained by the model (M_{model}) as a function of the experimental values ($M_{experimental}$). The regression of those data to a linear function (eq. (3.5)) results in three parameters that can be used to evaluate the description of the experimental values by the model, i.e. the linear slope (a, which must be as close as possible to one), the intercept (b, which must be as close as possible to zero) and the coefficient of determination (R^2; that must be as close as possible to one). It is a simple and efficient approach to evaluating the model fitting.

$$RMSD = \sqrt{\frac{\sum_{i=1}^{n}(M_{experimental} - M_{model})^2}{n}} \tag{3.3}$$

$$NRMSD = 100 \cdot \frac{RMSD}{(M_{experimental})_{maximun} - (M_{experimental})_{minimun}} \tag{3.4}$$

$$M_{model} = a \cdot M_{experimental} + b \tag{3.5}$$

3.2.3 Adsorption isotherms

Grains with different moisture contents (prepared using the procedure described above) were ground using a hammer mill prior to determining their water activity at 25°C using a water activity meter (AquaLab 4TE, Decagon Devices, Inc USA). The sample moisture content (% d.b.) was then plotted as a function of the water activity. The obtained curve was modeled using the Oswin Equation (eq. (3.6)) since it is recommended for starchy food (AL-MUHTASEB; MCMINN; MAGEE, 2002). In this equation, M is the moisture content of the product (% d.b.), a_w is the water activity of the product and A and B are model parameters related to the curve shape.

$$M = A\left[\frac{a_w}{1-a_w}\right]^B \tag{3.6}$$

3.2.4 Explanation of the Adzuki beans hydration process

Three different treatments were performed in order to explain the Adzuki beans hydration phenomenon, comparing and relating the obtained hydration rates with the grain morphology and initial moisture content. Especially, the function of two tissues of the grain during the hydration process was studied: the seed coat and the hilum (Figure 3.2).

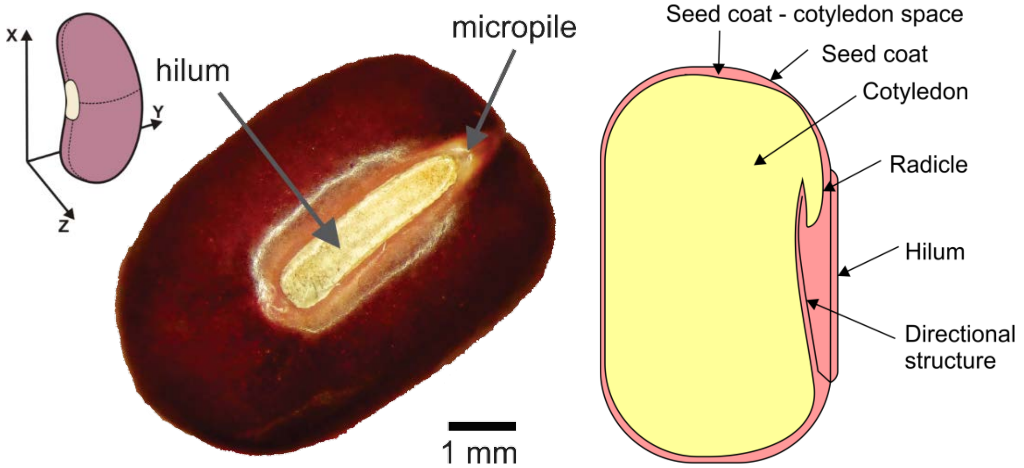

Figure 3.2 – External morphology (XZ plane) and internal morphology (YX plane) of Adzuki grain (*Vigna agularis*)

In the first treatment, the Adzuki beans were hydrated at M_N (14.96 %d.b.) without the seed coat, which was manually and carefully removed. In the second treatment, the hydration of the beans was carried out at a low initial moisture content (4.23 %d.b.), with their hilum covered with a contact glue (cyanoacrylate ester glue – Loctite Super Bonder®, Henkel Brazil). Finally, in the third treatment, the hydration of the beans was carried out at a high initial moisture content (29.24 %d.b.), also covering their hilum.

Further, the grain structure evaluation was performed by a microstructural analysis (using a scanning electronic microscope - SEM) and X-ray analysis, in order to explain the hydration process.

For the microstructural analysis, the samples were cut with a scalpel blade in order to see the different tissues (seed coat, cotyledon, and external surface) and dehydrated in a sealed container using silica gel for 3 days. Then, they were sputtered with a 30 nm gold layer. Finally, the samples were observed in a scanning electronic microscope operated at an acceleration voltage of 15 kV (LEO 435 VP, Leo Electron Microscopy Ltd., Cambridge, England).

For X-ray analysis, twelve grains were X-rayed using a model MX-20 DC-12 digital Faxitron X-ray connected to a computer, exposing them to the radiation at 20 kV for 10 s. The grain (at M_N) was X-rayed at 0, 1, 2, 4 and 6 h of hydration at 35°C.

3.3 Results and Discussion

3.3.1 Hydration process

Adzuki beans showed a sigmoidal behavior hydration at the moisture content in equilibrium with the environment (M_N) (14.96 % d.b.; Figure 3.3) and needed more than eight hours to reach the equilibrium moisture content at 35 °C. Therefore, it is highlighted that the hydration process is mainly a discontinuous and slow unit operation in the industrial process. Consequently, a structure evaluation was carried out in order to explain this process.

Figure 3.4-A shows the hydration of Adzuki beans with and without its seed coat. It can be seen that the seed coat is the main cause of the slow water intake and the low water holding capacity, defining the sigmoidal behavior during hydration.

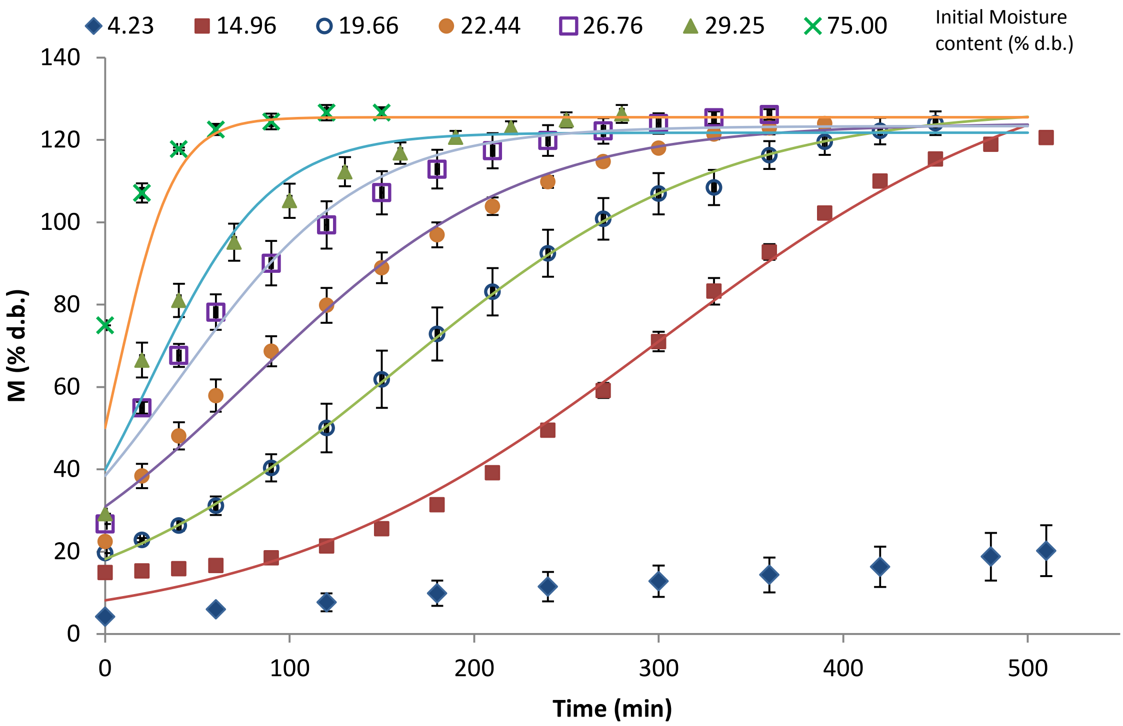

Figure 3.3 – Adzuki grains hydration at 35°C as function of its initial moisture content. The dots are the experimental values; the vertical bars are the standard deviation and the curves are the Kaptso et al. Model (eq. (3.1))

Further, the seed coat was not demonstrated as the only pathway for the water ingress during the hydration process. The hilum structure is also an important route. Figure 3.4-B shows the results of two special treatments that helped to explain the principal function of the seed coat and hilum during the water uptake in Adzuki beans. When the hilum was covered in the grains at M_N (14.96 % d.b), the grains practically did not hydrate, indicating the high impermeability of the seed coat, and also highlighting that the hilum was the main route to the water intake in this condition. It means that the seed coat was impermeable when the grains had a moisture content below the critical one (lower than 20% d.b.). In fact, those grains were soaked for two more days and they still did not hydrate.

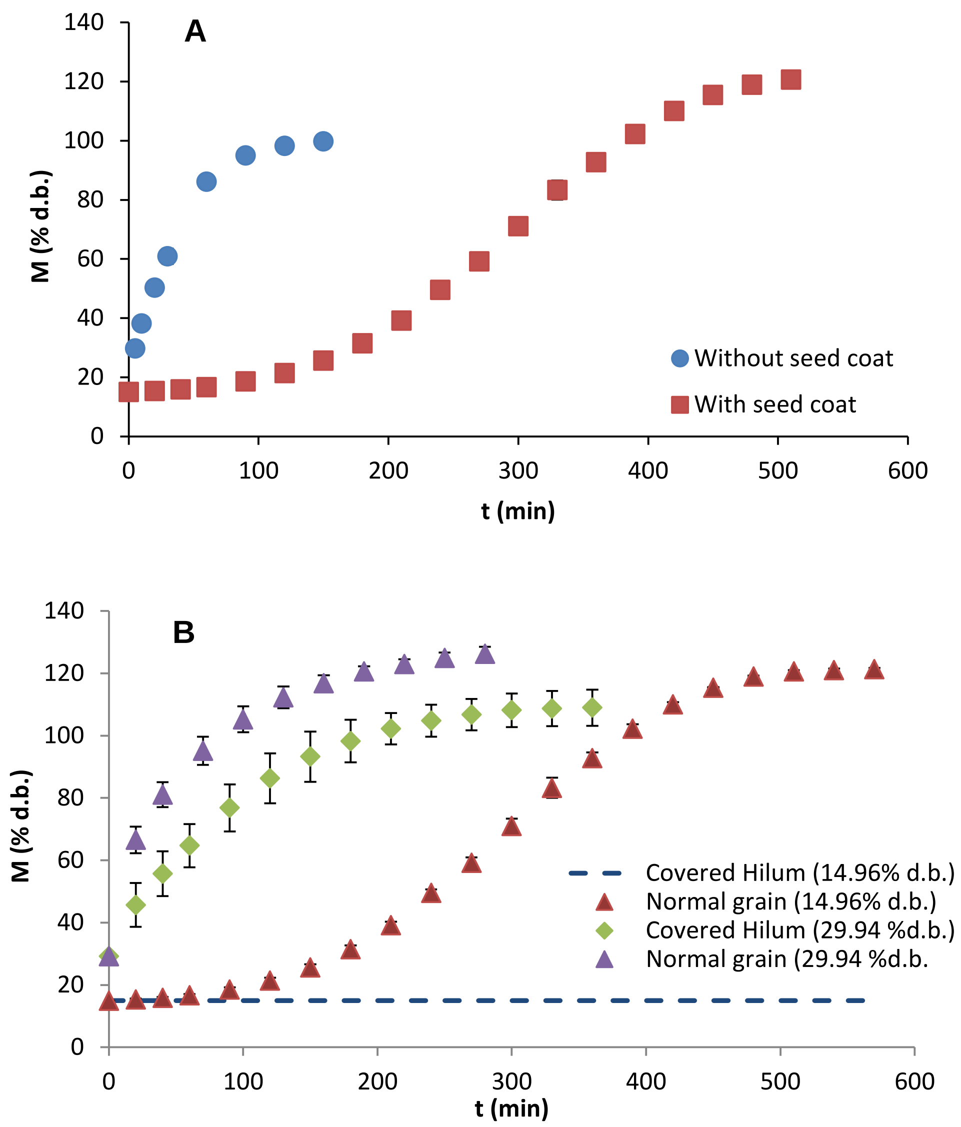

Figure 3.4 – Treatments to explain the function of the Adzuki grain structures on the hydration process (35 °C). The dots are the experimental values; the vertical bars are the standard deviation. (A) Hydration of Adzuki grains at M_N (14.96 %d.b.) with and without its seed coat. (B) Hydration of Adzuki grains at different initial moisture content to explain the function of the seed coat and the hilum on the hydration process. Due to its negligible hydration up to 48 h, the sample with 14.96% of initial moisture content and with its hilum covered is represented by a dashed curve

On the other hand, when the hilum was covered at a moisture content higher than the critical one (at 29.94 % d.b.), the water entered into the grain, but in a slower rate than the normal (uncovered) grains (Figure 3.4-B). It demonstrates that the seed coat permeability is function of the grain moisture, and that the hilum still exerts an important function even though the higher moisture content of the grains.

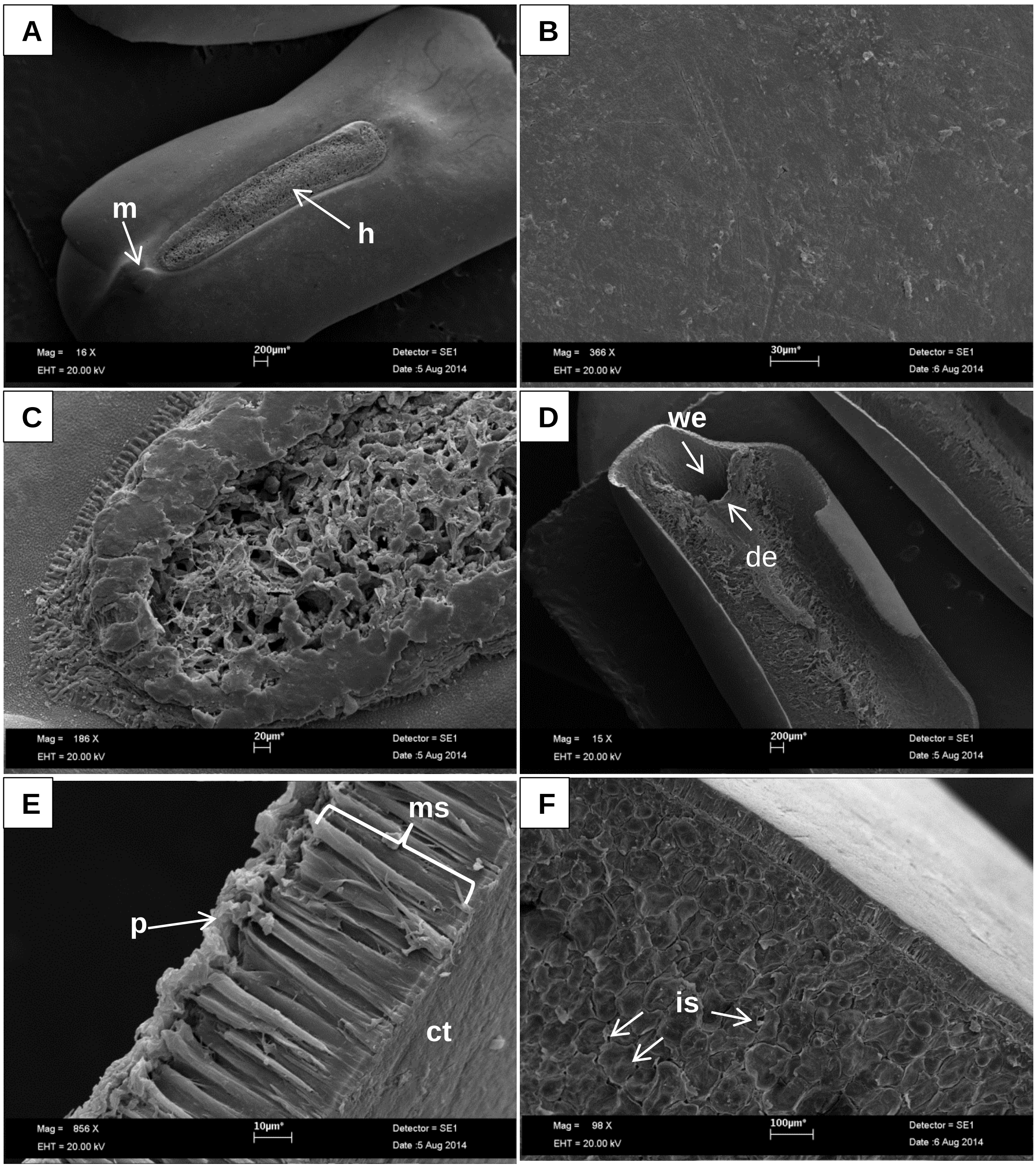

Figure 3.5 – Adzuki grain microstructure (SEM, 20 kV; the magnifications are shown in the figures). A. Grain: mi. micropile, hi. Hilum; B. Seed coat external surface. C. Hilum. D. Hilum view from the inside: we. water entrance, de. directional structure. E. Seed coat: ct. cuticle, ms. macroesclereids cells, p. parenchyma. F. Cotyledon: is. Intercellular spaces

Figure 3.5 shows the microstructure of the principal tissues of Adzuki bean. It can be seen that the seed coat is little or almost not porous (Figure 3.5-B, Figure 3.5-E), in contrast to the hilum which is very porous (Figure 3.5-C). Consequently, at M_N (14.96 %d.b.), the water enters principally by the hilum, and then, a directional structure (Figure 5D) guides it to firstly hydrate the radicle. Once the water reaches the radicle, the water starts to be distributed to the seed coat-cotyledon space. This is the slowest step since the seed coat-cotyledon space is very small (Figure 3.5-F) and the water influx is practically only through the hilum. When the seed coat reaches a particular moisture content, it starts to let water to pass into the grain, contributing to the hydration process. The structure of the seed coat is very compact and it is only formed by a macroesclereids layer and a thin layer of parenchyma (Figure 3.5-E) controlling the entrance of the water (BORGUETTI, 2008). The cotyledon of Adzuki beans is more easily hydrated since it has many intercellular spaces where the water can be easily distributed by capillarity (Figure 3.5-F).

Figure 3.6 shows the radiographs of Adzuki beans at different hydration times at 35°C. It can be observed that the seed coat-cotyledon space near the hilum increased during the six first hours of hydration, demonstrating that the water entered by the hilum in the first phase of the hydration process. According to the hydration curve at M_N (Figure 3.3), at 6 h of hydration, the grains raised the inflexion point. This is in agreement with the radiographs results. After this time, the water was distributed to the cotyledon until reaching the equilibrium moisture content, and the hydration behavior turned into a DCS shape. It should be mentioned that the volume of the grains did not increase during the first six hours of the process; however, after the inflexion point of the curve, it started to increase. The volume increment means that the water was entering to the cotyledon, which started to increase its volume.

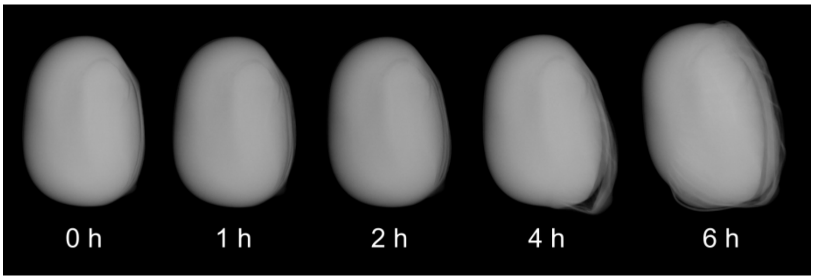

Figure 3.6 – Radiography of Adzuki bean (YX plane) at different hydration times (14.96 % d.b. and 35°C)

3.3.2 Effect of the initial moisture content

When the initial moisture content of the grain was increased, the lag phase of the sigmoidal behavior decreased until it disappeared at 22.44 % d.b. In this condition, the grain behavior changed from the sigmoidal to the DCS behavior. It means that the hydration behavior depends on the initial moisture content of the grain. Further, when the grains, at lower initial moisture content (4.23 %d.b.), were soaked, the hydration was too slow that they did not reach even the 20% of the equilibrium moisture content after 8 h.

By evaluating these results, there probably exists a “critical” initial moisture content where the hydration behavior changes. In fact, it may be related with the corresponding water activity (a_w), and the consequent grain morphological changes. For example, the seed coat permeability change.

The reasons for the seed coat permeability increase with increasing moisture content can be described as follows. The permeability of the seed coat depends on its physical chemical characteristics since its component’s organization and properties can change with the different moisture contents.

The adsorption isotherm of Adzuki beans is shown in Figure 3.7 and represented by eq. (3.7) (R^2=0.985). It is interesting to note that the initial moisture content, where the hydration behavior changes is between 19.66 %d.b. and 22.44 %d.b., the same region where the adsorption isotherm shows the change of the water from the zone II to the zone III (REID; FENNEMA, 2008).

$$M = 9.748 \cdot \left(\frac{a_w}{1-a_w}\right)^{0.461} \qquad (3.7)$$

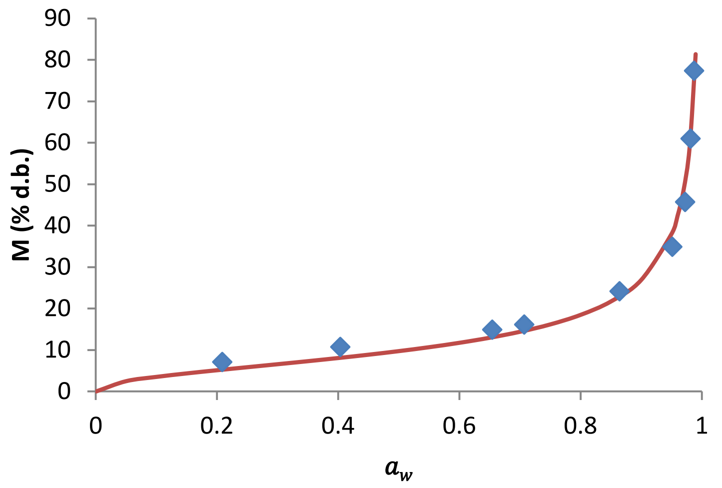

Figure 3.7 – Adsorption isotherm of Adzuki grains (25ºC). The dots are the experimental values; the vertical bars are the standard deviation and the curve is the Oswin Model (eq. (3.7))

The application of the glassy state theory in grains can partially describe this relation (ROSS; ARNTFIELD; CENKOWSKI, 2013). This theory stated that there exists a condition (temperature or water activity – consequently, the moisture content) where the grain (especially the seed coat's components) passes from a glassy state to a rubbery state through a phase transition. During this phase transition, there are changes of the physical properties of foods during contact between water and hydrophilic ingredients (BELITZ; GROSCH; SCHIEBERLE, 2009). Near the junction of zones II and III of the adsorption isotherm, the amount of water is sufficient to lower the glass transition temperature of the hydrated macromolecules so the sample temperature and the sample glassy transition temperature are equal. In consequence, the addition of water (zone III) causes a glass–rubber transition in samples containing glassy regions (REID; FENNEMA, 2008) These changes on the seed coat components can affect the permeability of the structure.

The plasticizing effect takes place when the moisture content is increased at constant temperature or when the temperature is increased at constant moisture content (AL-MUHTASEB et al., 2002). In this study, the plasticizing of the seed coat took place through increasing of the initial moisture content. Therefore, when the initial moisture content passes ~20 % d.b., the seed coat permeability and the hydration behavior changed.

The lag phase appears, during the grain hydration. It is probably due to need for the seed coat to be saturated with the solvent (water) in order to pass from the glassy state to the rubbery state. When it happens, the lag phase ends and the hydration behavior changes from the sigmoidal to the DCS, as shown on Figure 3.3. It means that it is necessary to reach a certain quantity of energy to cause the phase change, for example, provided by a higher water soaking temperature (reducing lag phase, as in (OLIVEIRA et al., 2013)) or by increasing the water activity which involves the moisture content increase. As consequence, the grain behavior depends on the initial moisture content. Therefore, higher initial moisture content decreases the lag phase that disappears in certain moisture content when the seed coat is enough hydrated to continue the hydration following the DCS behavior.

In conclusion, the hydration mechanism of a grain with sigmoidal behavior has been firstly explained according to its initial moisture content and its morphology. Figure 3.8 shows a summary of the entire hydration process explained above. It was demonstrating that the mass transfer (water intake) is not a mere diffusional phenomenon in the grain's hydration; it is a complex process that depends on the physicochemical and morphology properties.

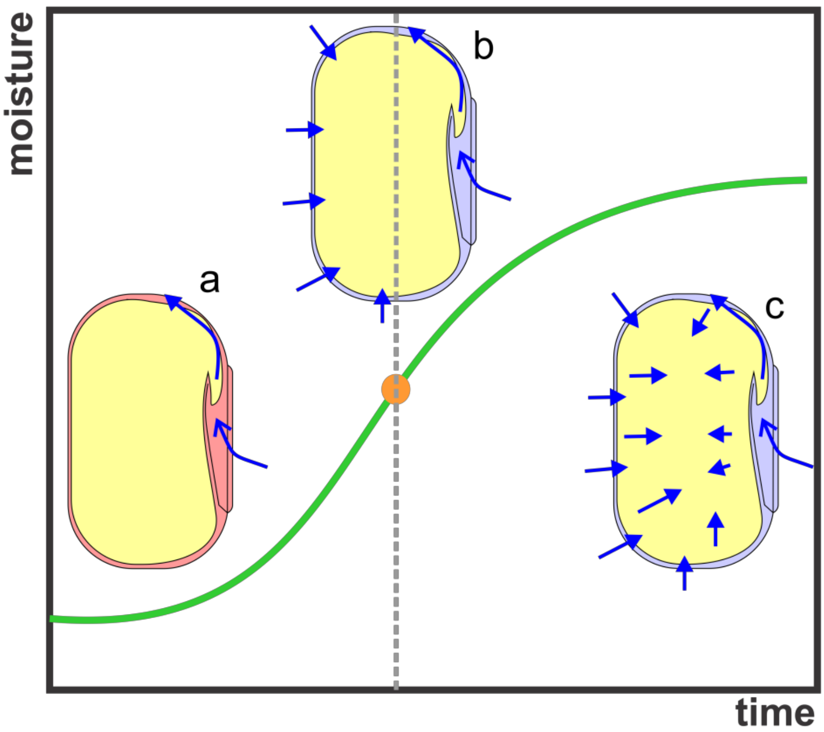

Figure 3.8 – Hydration mechanism of Adzuki bean: a. Water influx by the hilum and filling the seed coat–cotyledon space; b. The seed coat become permeable (inflexion point); c. Hydration of cotyledon

3.3.3 Mathematical modeling

The hydration kinetics of Adzuki beans at different initial moisture contents exhibited different behaviors. Below ~20 % d.b., the hydration kinetics had sigmoidal behavior and above that moisture content, it had DCS behavior. Therefore, it was used the Kaptso et al. Model (KAPTSO et al., 2008) to fit the data of sigmoidal behavior and the Peleg Model (PELEG, 1988) to fit the DCS data. The parameters of both models are shown in Table 3.1.

On the other hand, in order to obtain only one model to describe the grain hydration at all values of M_0, all the data were modeled using Kaptso et al. model since it can approximately fit the DCS data. It should be mentioned that the hydration kinetics at 4.23 % d.b. was not evaluated, as the grains took much longer than the other conditions to hydrate.

Table 3.1 – Calculated parameters of Kaptso et al. Model (eq. (3.1); (KAPTSO et al., 2008)) and Peleg Model (eq. (3.2); (PELEG, 1988)) for each evaluated initial moisture content

M_0 (%d.b.)	Kaptso et al. Model				Peleg Model		
	Meq (%d.b.)	τ (min)	k_K (min^{-1})	R^2	k_1 (min. (%d.b.$^{-1}$)	k_2 (%d.b.$^{-1}$)	R^2
4.23	*	*	*	*	*	*	*
14.96	143.19±3.18	301.52±9.91	0.0093±0.0004	0.99	*	*	*
19.66	128.17±3.61	157.84±17.92	0.0114±0.0011	0.99	*	*	*
22.44	124.11±2.22	79.96±11.35	0.0138±0.0008	0.99	1.308±0.216	0.0062±0.0007	0.99
26.76	123.38±1.69	39.69±4.20	0.0200±0.0034	0.98	0.657±0.100	0.0081±0.0002	0.99
29.25	121.77±2.00	23.7±4.20	0.0304±0.0052	0.97	0.414±0.084	0.0088±0.0004	0.99
75.00	125.52±1.91	6.38±0.36	0.0642±0.0076	0.99	0.257±0.043	0.0173±0.0010	0.99

* : Undetermined parameters

The Kaptso et al. Model has three parameters: the equilibrium moisture content (M_{eq}), the water absorption rate parameter (k_k) and the parameter that describe the inflection point in the curve (τ). Therefore, the effect of the initial moisture content on those parameters was studied.

The value of the parameter k_k exhibited sigmoidal behavior as a function of initial moisture content (Figure 3.9). This parameter is constant until the initial moisture content reaches ~ 20 %, d.b. Then, it rapidly increases until a certain initial moisture content where the maximum is reached and this parameter becomes constant again. Consequently, when the grains initial moisture content is higher than ~20 % d.b., the water absorption rate is higher, reflecting the change on the seed coat permeability. Further, it is necessary to complete the hydration of the seed coat by filling the seed coat-cotyledon with water, which it is a very slow process reducing the general water absorption rate. Consequently, the first plateau of the parameter k_k behavior is related to the water flow through the hilum, while the rest of the curve is related to the water flow through the hilum and the seed coat at the same time.

For modeling this parameter, and due to the observed behavior (Figure 3.9), a mathematical function, which describes a sigmoidal change between the known minimum and maximum values (eq. 3.8), was used. This model fitted very well (R^2=0.99).

$$k_k = 0.008663 + \left(\frac{0.05633}{1+53587\cdot 10^5 \cdot M_O^{-6.4961}}\right) \quad (3.8)$$

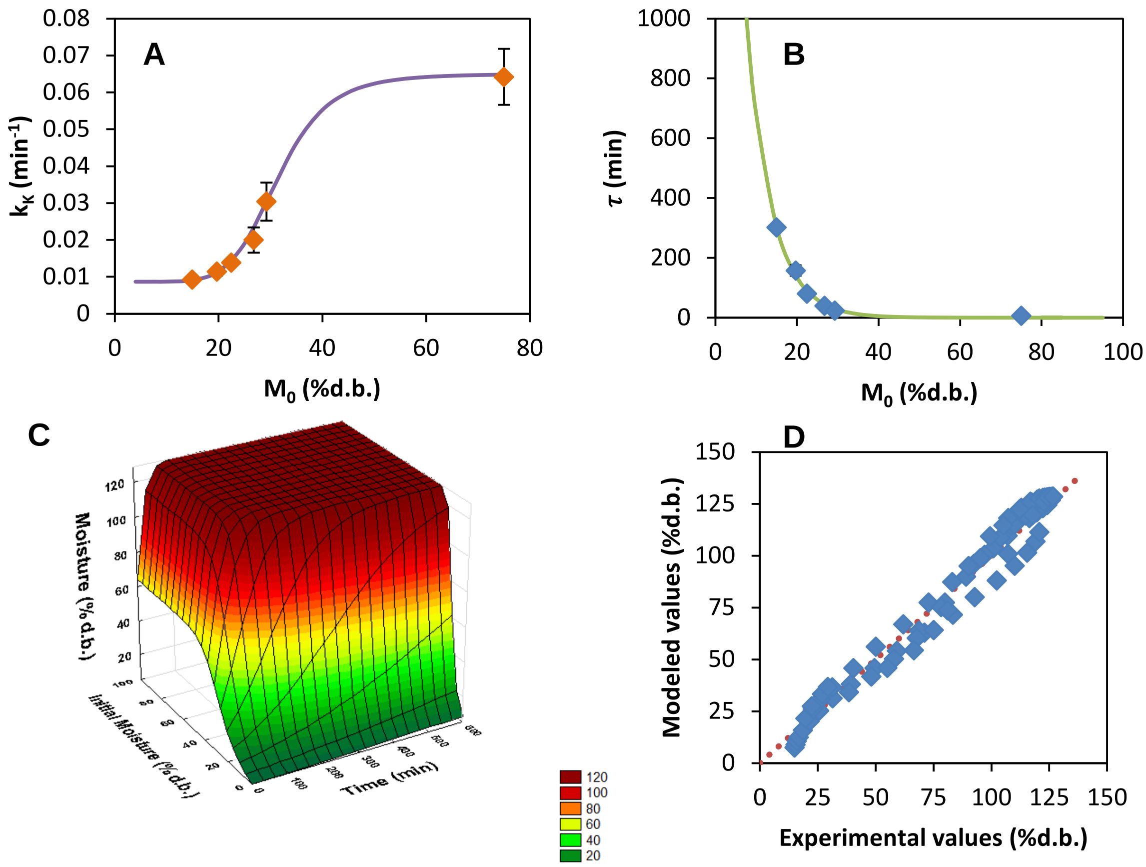

Figure 3.9 – Parameters $\boldsymbol{k_k}$ (A) and $\boldsymbol{\tau}$ (B) of the Kaptso et al. Model (eq. (3.1)) as function of the grain initial moisture content. The dots are the experimental values; the vertical bars are the standard deviation and the curves are the model of eq. (3.8) and eq. (3.9). (C) General model that describes the moisture content of adzuki grains as function of time of immersion and the initial moisture content of the grain (eq. (3.10)). (D) Experimental values modeled values (eq. (11)); the dashed line represents a regression with a = 1, b = 0 and R^2 = 1

The value of the parameter τ, which is related to the length of the lag phase, exhibited an exponential decay in relation to the initial moisture content of the grain (Figure 3.9). The value of this parameter tends to zero when the initial moisture content of the grains is above ~20 % d.b. since the lag phase of the hydration process disappears. In contrast, below this initial moisture content, the τ value exponentially increases, which means that the seed coat permeability is greatly reduced. In fact, when the grain at 4.23 % d.b. was soaked, the hydration was so slow that it did not reach even the 20% equilibrium moisture content after 8 h. Due to the observed behavior, an exponential function was used to model it (eq. (3.9), R^2=0.99).

$$\tau = 3424.67 \cdot e^{-0.1617 \cdot M_o} \tag{3.9}$$

The equilibrium moisture content (Meq) of all experiments was practically the same, and it was considered that the initial moisture content of the grains did not affect the equilibrium moisture content, but only the water uptake kinetics (which, in fact, is to be expected). Consequently, it was considered the average equilibrium moisture (128.5 ± 2.43 % d.b.) for the general model.

Finally, a general model was sought to obtain the moisture content of the Adzuki beans as function of both initial moisture content ($14 < M_o(\% \, d.b.) < 70$) and time of soaking (in min). This model is shown in eq. (3.10) with an R^2=0.97. Moreover, the model was plotted in a 3D surface, being shown on Figure 3.9. The surface highlights the initial moisture content when the hydration behavior changes from the sigmoidal shape to the DCS.

$$M(t, M_o) = \frac{128.5}{1+\exp\left(-\left(0.008663+\left(\frac{0.05633}{1+53587 \cdot 10^5 \cdot M_o^{-6.4961}}\right) \cdot \left(\mathrm{t}-3424.67 \cdot \exp(-0.1617 \cdot M_o)\right)\right)\right)} \tag{3.10}$$

The values obtained by the model (eq. (3.10)) were then plotted with the experimental ones in order to verify the goodness of fit. A well-fitted linear equation (eq. (3.11), R^2 = 0.974) was obtained that demonstrated it can be successfully used to predict the moisture content of Adzuki beans. Therefore, the parameters a and b from eq. (3.5) were statistically equal to one and zero, respectively (p-values are 0.064 and 0.120, respectively) (eq. (3.11) and Figure 3.9), reinforcing that the proposed model can be successfully used to predict the moisture content as function of the initial moisture content and the time. In addition, the root-mean-square deviation (RMSD) and the normalized RMSD (NRMSD) values were calculates being 6.49 %d.b. and 5.37 % respectively, also highlighting the goodness of fitting.

$$M_{model} = 1.0351 \cdot M_{experimental} + 2.7138 \tag{3.11}$$

Consequently, for process engineering purposes, the Adzuki beans hydration behavior can be described by eq. (3.10).

3.4. Conclusions

By combining and relating the grain’s morphology, initial moisture content and hydration rates, the Adzuki bean (*Vigna angularis*) hydration phenomenon could be properly described. It was demonstrated that the initial moisture content affects the grain's hydration behavior. The process showed a sigmoidal behavior at initial moisture contents below ~20 % d.b. and a DCS behavior above that initial moisture content. This behavior was attributed to changes in the seed coat permeability. The water mainly enters into the grain by the hilum at moisture contents below the critical one, since the seed coat is impermeable. The seed coat becomes permeable when the initial moisture content is above ~20 % d.b. The Kaptso et al. Model (eq. (3.1)) fitted the data very well at the different initial moisture contents, obtaining the relation of each parameter as function of the initial moisture content. The water absorption rate (k_k) exhibited a sigmoidal increasing behavior; the time to rise to the inflexion point was related to the lag phase of the hydration (τ). It showed an exponential decay; the equilibrium moisture constant (M_{eq}) was considered constant at all initial moisture contents. Finally, a general model was derived, which can be used to predict the moisture content of Adzuki beans as function of the initial moisture content of the grains and time. Consequently, this work can help to understand and to enhance the hydration process of the grains.

Acknowledgments

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4 MECHANISMS FOR IMPROVING MASS TRANSFER IN FOOD WITH ULTRASOUND TECHNOLOGY: DESCRIBING THE PHENOMENA IN TWO MODEL CASES[1]

Abstract

The aim of this work was to demonstrate how ultrasound mechanisms (direct and indirect effects) improve the mass transfer phenomena in food processing, and which part of the process they are more effective in. Two model cases were evaluated: the hydration of sorghum grain (with two water activities) and the influx of a pigment into melon cylinders. Different treatments enabled us to evaluate and discriminate both direct (inertial flow and "sponge effect") and indirect effects (micro channel formation), alternating pre-treatments and treatments using an ultrasonic bath (20 kHz of frequency and 28 W/L of volumetric power) and a traditional water-bath. It was demonstrated that both the effects of ultrasound technology are more effective in food with higher water activity, the micro channels only forming in moist food. Moreover, micro channel formation could also be observed using agar gel cylinders, verifying the random formation of these due to cavitation. The direct effects were shown to be important in mass transfer enhancement not only in moist food, but also in dry food, this being improved by the micro channels formed and the porosity of the food. In conclusion, the improvement in mass transfer due to direct and indirect effects was firstly discriminated and described. It was proven that both phenomena are important for mass transfer in moist foods, while only the direct effects are important for dry foods. Based on these results, better processing using ultrasound technology can be obtained.

Keywords: Ultrasound; Mass transfer; Micro channel; Sponge effect; Inertial flow

4.1 Introduction

Ultrasound technology has been widely studied as an alternative for improving food processing in such operations as defoaming, freezing, extraction, emulsification, hydration, drying and others (AWAD et al., 2012). In mass transfer unit operations, the ultrasound technology has been successfully used in different processes, such as extraction (RIERA et al., 2004), drying (AZOUBEL et al., 2010; CÁRCEL et al., 2011; RODRÍGUEZ et al., 2014), osmotic dehydration (GARCIA-NOGUERA et al., 2010), hydration (GHAFOOR et al., 2014; PATERO; AUGUSTO, 2015), and desalting (OZUNA et al., 2014).

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[1] This Chapter is currently under review:
MIANO, A.C.; IBARZ, A.; AUGUSTO, P.E.D. 2015. Mechanisms for improving mass transfer in food with ultrasound technology: Describing the phenomena in two model cases.

The enhancement of the mass transfer unit operation by ultrasound technology has been attributed to different mechanisms. These are considered direct and indirect effects of ultrasound. The direct effects are related to the “sponge effect” and inertial flux. When ultrasonic waves travel through the product, they cause a rapid alternating compression and expansion of the tissue matrix, which is compared to a sponge squeezed and released repeatedly (DE LA FUENTE-BLANCO et al., 2006; MULET et al., 2003; YAO; ZHANG; LIU, 2009). This phenomenon can keep micro channels and pores unobstructed, facilitating mass transfer (YAO et al., 2009). Further, it can promote mass flow due to pumping. However, although it is frequently attributed with these direct effects on the mass flow (AZOUBEL et al., 2010; FERNANDES et al., 2008; OZUNA et al., 2014; SABAREZ et al., 2012; YILDIRIM et al., 2011), these have not been demonstrated during food processing yet.

The indirect effect is related to micro channel formation due to the acoustic cavitation (CHEMAT; KHAN, 2011). When ultrasound waves travel through the product, the phenomenon of cavitation takes place in the water inside or outside the product cells, resulting in cell and tissue disruption and the consequent formation of cavities and micro channels. In fact, the micro channel formation due to ultrasound has been shown for different moist foods, such as melons, potatoes, strawberries, apples and cod (FERNANDES et al., 2008; GAMBOA-SANTOS et al., 2014; KARIZAKI et al., 2013; OZUNA et al., 2014; RODRÍGUEZ et al., 2014). Also, the presence of these micro channels is believed to be the main effect of the ultrasound technology in enhancing the mass transfer phenomena in food processing (GARCIA-NOGUERA et al., 2010; OZUNA et al., 2014; PATERO; AUGUSTO, 2015; RODRIGUES; FERNANDES, 2007). However, the formation of micro channels and its importance for mass flow has not been studied for dry foods, such as grains. As the water activity of these products is low, the lower water vapor pressure can limit cavitation phenomenon, reinforcing the need for evaluation.

Consequently, this work aimed to demonstrate how these mechanisms improve the mass transfer phenomena in food processing, and in which part of the process they are more effective in. Therefore, two model cases were evaluated: the hydration of sorghum grain and the influx of a pigment into melon cylinders.

4.2 Materials and Methods

The mechanisms of ultrasound enhancement during mass transfer processes were studied in two kind of food: sorghum grains (representing dry foods, with low water activity) and yellow melon cylinders (representing moist foods, with high water activity). Moreover, these two foods have already shown good results when treated with ultrasound during osmotic dehydration (FERNANDES et al., 2008) and hydration (PATERO; AUGUSTO, 2015).

During the experiments, an ultrasonic bath a frequency of 40 kHz and a volumetric power of 28 W/L (USC-1400, Unique Brazil) was used. This bath has its piezoelectric elements arranged below the tub. These generates the mechanical waves that are transmitted through the water (or solution), reaching the product. The volumetric power was determined following the method described by TIWARI et al. (2008), and it was the same or very close to that used in previous works (PATERO; AUGUSTO, 2015; YILDIRIM et al., 2011). The temperature of the water was controlled using a stainless steel heat exchanger coupled to an external water bath, which was placed at the top of the solution inside the ultrasonic water bath.

4.2.1 Ultrasound mass transfer enhancement on grains

For sorghum grains, the hydration process was chosen as the evaluated mass transfer processing.

Sorghum grains (Sorghum bicolor) with water activity of 0.653±0.001 and a moisture content of 12.46±0.17 % d.b. (g water / 100 g of dry matter) were used. Furthermore, in order to prepare a sample with higher water activity (0.985±0.003) the grains were hydrated for 3 hours at 25 °C. Then, these grains were superficially dried and put into sealed containers for two days at 5ºC in order to homogenize the moisture. Consequently, the evaluation was carried out using two different conditions of water activity.

Different treatments were performed in order to identify the mechanism of mass transfer enhancement caused by the ultrasound technology (Figure 4.1). These treatments helped to differentiate the indirect effects (micro channels formation) with the direct effects (the sponge effect, inertial flow), as well as the moment these acted during processing.

Three treatments were performed for the low water activity grains:

- Treatment 1 (TS1: H) consisted of hydrating the grains (15 g of grains in a beaker with 2 L of distilled water) without the application of ultrasound at 25 °C throughout the process (2 h).
- Treatment 2 (TS2: PUS / H) consisted of vacuum packing one layer of sorghum grains in order to treat the grain with ultrasound without it becoming hydrated. This pack was placed at the bottom of the water bath to receive the sound waves better. After 3 h of pretreatment, the grains were unpacked and hydrated (beaker with 2 L of distilled water) without ultrasound application at 25 °C for 2 h.
- Treatment 3 (TS3: H+US) consisted of hydrating the grains (15 g of grains in the ultrasonic bath with 2 L of distilled water) with the application of ultrasound at 25 °C throughout the process (2 h).

Four treatments were performed for the high water activity grains. Treatments 1, 2 and 3 were the same as those applied to the low water activity grains. The other was:

- Treatment 4 (TS4: PUS / H+U) consisted of pretreating the grains, as in treatment 2, but, after that, hydrating them (15 g of grains in the ultrasonic bath with 2 L of distilled water) with the application of ultrasound at 25 °C for 2 h.

During the hydration process, the samples were periodically drained, superficially dried and their moisture content was obtained by mass balance. The sampling was carried out each 15 min for 2 h. All the treatments described above were performed in triplicate. The results were presented as the mean and the standard deviation.

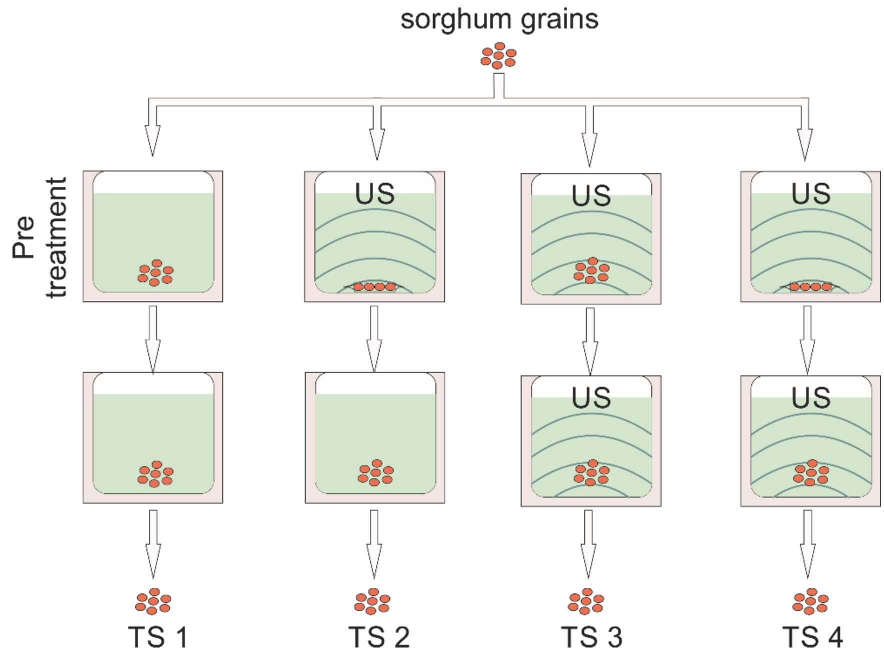

Figure 4.1 – Treatments to differentiate the ultrasound mechanisms (direct and indirect effects) that enhance mass transfer on the sorghum grains

4.2.2 Ultrasound mass transfer enhancement on melon cylinders

The effect of ultrasound processing on the mass transfer phenomena of foods was studied by considering a pigment transfer into canary melon (*Cucumis melo inodorus*) cylinders (89.6±0.6 %w.b. of moisture, 9.4±0.5 °Brix and 5.74±0.08 of pH). The melon was cut into cylinders in order to obtain homogeneous and uniform specimens.

By evaluating pigment flow into the cylinders in processes under ultrasound, without ultrasound and with a pre-treatment using ultrasound, it was possible to evaluate the direct effects of ultrasound (sponge effect, inertial flow) and those related to the changes in the product microstructure caused by the acoustic cavitation (micro-channels formation; indirect effects).

Melon cylinders of 4 cm long and 1.5 cm in diameter were obtained using a fruit corer. For some treatments (Figure 4.2; explanation as follows), the cylinders were perforated using a 0.3 mm-diameter needle. 50 perforations were done randomly along the cylinder, and in the direction of its diameter. The cylinders were perforated in order to simulate higher porosity generated by the micro channels formation and to discriminate the direct effects (i.e., to guarantee samples with micro channels and then evaluate their behavior during processing, in order to compare it with the other treatments).

Ten cylinders were immersed in a beaker or in the ultrasonic bath (depending on the treatment) with 2 L of brilliant blue (food grade, kindly donated by SanLeon, Brazil, www.sanleon.com.br) solution (0.0625 g/L) at 25ºC for the mass transfer evaluation. Six different treatments were considered in order to discriminate the ultrasound effects on the mass transfer process. The treatments are shown in Figure 4.2:

- Treatment 1 (TM1: PS) consisted of immersing the cylinders in the pigment solution without ultrasound application throughout the process (2.5 h).
- Treatment 2 (TM2: PS+US) consisted of immersing the cylinders in the pigment solution with ultrasound application throughout the process (2.5 h).
- Treatment 3 (TM3: W / PS) consisted of immersing the cylinders in distilled water without ultrasound application for 60 minutes as a pretreatment. Then, the process continued in the pigment solution without ultrasound for 1 h.
- Treatment 4 (TM4: W+US / PS) consisted of immersing the cylinders in distilled water with ultrasound application for 60 minutes as a pretreatment. The process then continued in the pigment solution without ultrasound for 1 h.
- Treatment 5 (TM5: P / PS) consisted of immersing the perforated cylinders in the pigment solution without ultrasound application throughout the process (1 h).
- Treatment 6 (TM6: P / PS+US) consisted of immersing the perforated cylinders in the pigment solution with ultrasound application throughout the process (1 h).

The mass transfer process was evaluated for 2.5 hours, removing one cylinder each 30 minutes for treatments 1 to 4. For treatments 5 and 6, the mass transfer process was evaluated for 1 hour removing one cylinder each 15 minutes. The removed cylinders were quickly washed with distilled water, drained and superficially blotted with absorbent paper before evaluation. Then, 2 g of the cylinder (after discarding its edges) was triturated with 8 mL of distilled water using a Ultra Turrax homogenizer (IKA® T25D, Brazil) for 30 s at 104 RPM, and then filtered with Whatman grade 2 filter paper. The filtered absorbance at 630 nm of wavelength (maximum absorbance of the pigment solution) was obtained for each cylinder using a spectrophotometer (Femto 600S, Brazil). Following the Beer-Lambert Law, the higher absorbance was considered as the higher pigment solution concentration in the cylinders. All the treatments described above were performed in triplicate. The results were presented as the mean and the standard deviation.

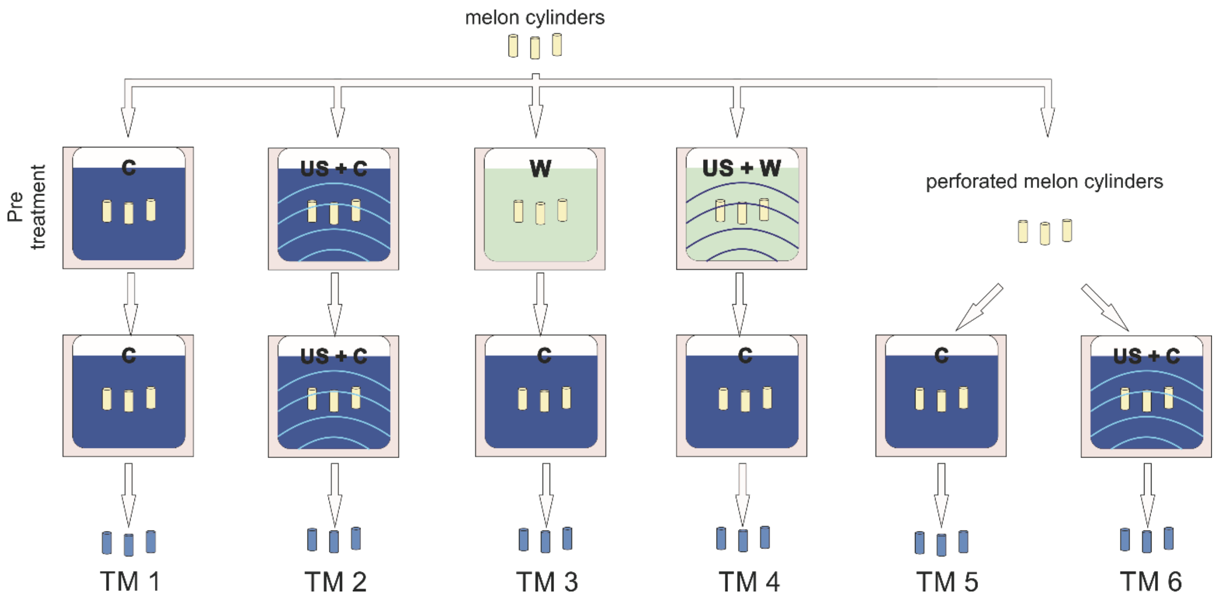

Figure 4.2 – Treatments for differentiate the ultrasound mechanisms (direct and indirect effects) that enhance mass transfer on the melon cylinders

4.2.3 Micro channels formation observation

In order to evaluate the formation of micro channels due to ultrasound technology, cylinders of agar gel (2 %; Oxoid - Thermo Fisher Scientific, Inc. USA) 4 cm long and 1.5 cm in diameter) were considered as model foods. They were treated with ultrasound in 2 L of brilliant blue solution (0.0625 g/L) at 25 ºC for 2.5 h (the same time as the melon cylinder treatments). This was carried out to obtain images for better visualization. The cylinders were placed in a black background illuminated from the side with a LED Flashlight and the images were obtained using a regular digital camera.

4.3 Results and Discussion

4.3.1 Ultrasound mass transfer enhancement in grains

Figure 4.3 shows the application of the ultrasound technology as a treatment and as pretreatment to the sorghum grains, representing a food with low water activity. As expected, when the grains were hydrated in the ultrasonic bath during all the process (TS3), the water intake was improved compared with the conventional hydration process (TS1) (PATERO; AUGUSTO, 2015). In contrast, when the packaged grains were treated with 3 hours of ultrasound and then hydrated without it (TS2), they did not hydrate faster than with the conventional process (TS1). These three treatments demonstrated that ultrasound technology does not generate micro channels in sorghum grains under conditions of water activity (0.6533±0.0004), or at least, this generation is negligible. The low vapor pressure of the water in grains hinders cavitation because the cavitation bubbles contain less vapor from the solvent (MASON; TIMOTHY; PETERS, 2004). That is why it is difficult for the micro channels to form inside the product by cavitation. It means that, at this water activity, ultrasound enhanced sorghum grain hydration due to direct effect that caused water to enter by inertial flow and/or the sponge effect.

On the other hand, when the same treatments were performed in sorghum grains with a higher water activity (0.9851±0.0029), different results were obtained. Figure 4.4 shows that when ultrasound is applied as a pretreatment (TS2) and the grains are then conventionally hydrated, there is an improvement in the hydration process. Micro-channel formation during the pretreatment was demonstrated, and this improved the mass transfer by reducing internal resistance. In contrast to the low water activity grains, the higher vapor pressure of the water facilitated cavitation and the formation of micro-channels, probably by cell disruption and matrix rupture.

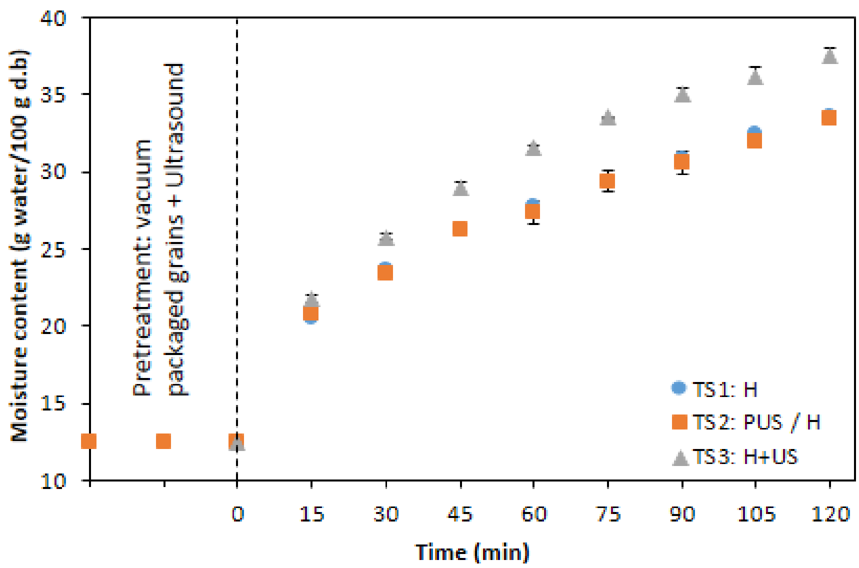

Figure 4.3 – Results of the treatments 1, 2 and 3 on the hydration of sorghum grains with low water activity (0.653±0.000) (H: conventional hydration process; PUS: pretreatment with ultrasound; H+US: ultrasound assisted hydration process. The slash means that a pretreatment was used). The dots are the average of the experimental values and the vertical bars are the standard deviations

Furthermore, when the hydration of the high water activity sorghum grains was assisted with the ultrasound technology (TS3), there was no improvement in the early stages, but the water intake began to increase with the process time. Although these sorghum grains had the right conditions to be affected by cavitation (high water activity) and to form micro channels, a certain process time was necessary for this to be effective. Apparently, acoustic cavitation occurs randomly inside the food matrix, causing the formation of micro cavities, which grow in size with the passing of time. They start to form cavities with different tortuosity and permeability. Many of these cavities can lack connection between each other or with the external medium, thus not improving or only slightly improving the mass transfer. Finally, the mass transfer phenomena are improved when a reasonable number of cavities are formed and/or when there are connections between those and the external medium, forming channels.

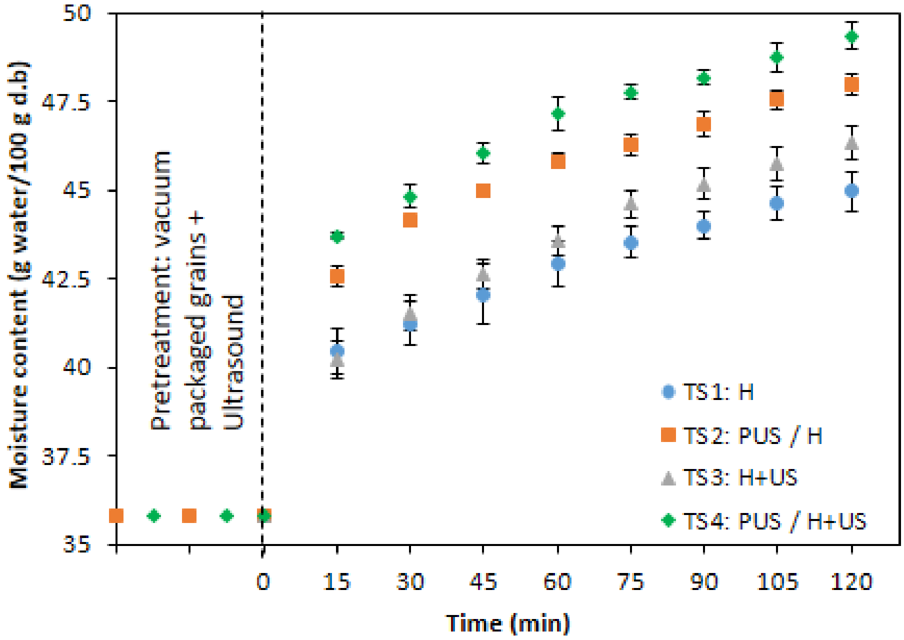

Figure 4.4 – Results of the treatments 1, 2, 3 and 4 on the hydration of sorghum grains with high water activity (0.985±0.003) (H: conventional hydration process; PUS: pretreatment with ultrasound; H+US: ultrasound assisted hydration process. The slash means that a pretreatment was used). The dots are the average of the experimental values and the vertical bars are the standard deviations

Cylinders of agar gel were used to try to see the micro-channel formation, and these were treated with and without ultrasound technology (Figure 4.5). The formation of different kind of cavities by ultrasound technology was observed, confirming the statement above (Figure 4.6). The different kind of cavities and micro channels formed can have varied tortuosity, permeability and diffusion, improving or not the mass transfer in different ways (WARNING et al., 2014).

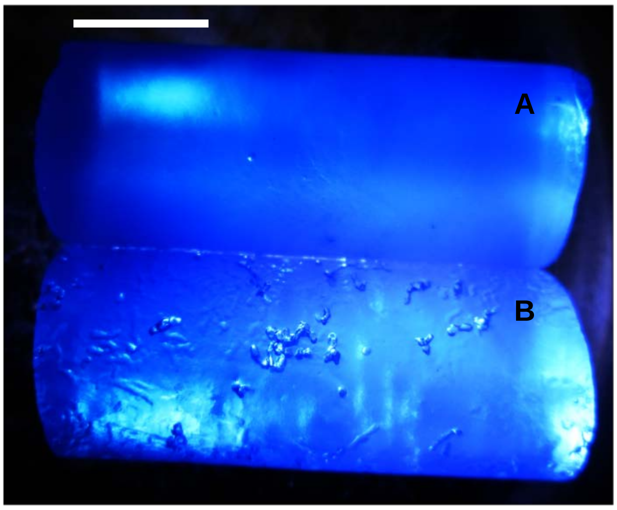

Figure 4.5 – Agar gel cylinders treated without ultrasound (A) and with ultrasound (B). The white bar is equivalent to 1 cm

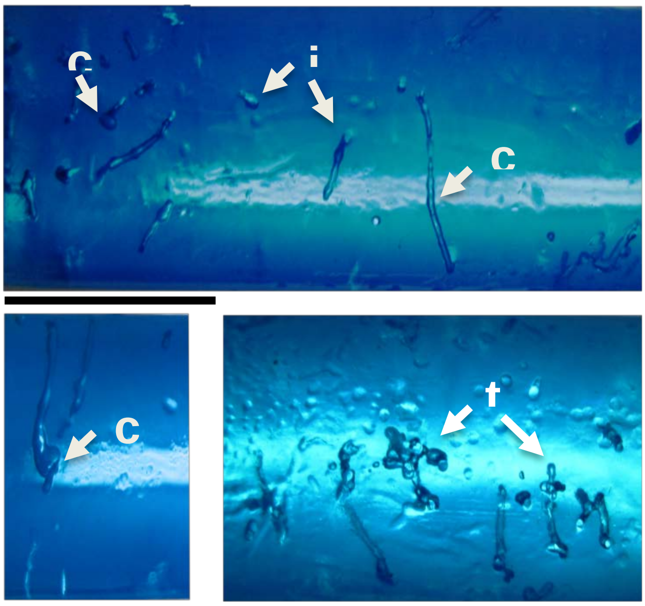

Figure 4.6 – Different kind of cavities and micro channels: tortuous (t), isolated cavities with lack of connectivity (i), and with external medium connectivity (c). The black bar is equivalent to 1 cm

Finally, treatment 4 (TS4), which consisted of hydrating the sorghum grains using the ultrasound technology after the pretreatment with ultrasound, showed an even better hydration rate than treatment 2 (TS2), which consisted of hydrating the grains without using the ultrasound technology after the pretreatment with ultrasound.

It not only proves that micro channels form, but also the direct effects (inertial flow and “sponge effect”) were important for enhancing mass transfer. Moreover, it means that the higher porosity of the grain, caused by micro-channel formation, enhance the direct effects of the ultrasound.

Based on these results, ultrasound-assisted hydration of grains can be explained.

When a grain is hydrated, firstly, the enhancement caused by the ultrasound technology is due to the direct effects (inertial flow and “sponge effect”). Then, from a certain water activity, the formation of micro channels starts to take place, further improving mass transfer. This explains why the enhancement of the hydration process is higher after a certain processing time than in the early stages. The few studies of ultrasound assisted grain hydration confirm this (GHAFOOR et al., 2014; PATERO; AUGUSTO, 2015; YILDIRIM et al., 2011), and it can be seen that the differences between the hydration curves grow wider as the process time passes.

Furthermore, these results highlight that the effect of applying the ultrasound technology is probably higher in products with higher water activity. Consequently, the use of this technology in food processing could be designed to maximize its effects, for example, by applying it only at some stages of the process.

Finally, it is important to highlight that the obtained results can only be directly applied for sorghum grains at this level of ultrasonic volumetric power. Each grain has its own structure and composition, which can be differently affected by the ultrasound technology. Further, different volumetric powers can change the relative importance of each mechanism during the ultrasonic processing. Despite this, the main qualitative finds of the present work can be generally interpreted.

4.3.2 Ultrasound mass transfer enhancement in melon cylinders

Figure 4.7 shows the results of the treatments 1 (TM1), which consisted of immersing the melon cylinders in the pigment solution without ultrasound, and 2 (TM2), which consisted of immersing the melon cylinders in the pigment solution with ultrasound. These treatments showed that the ultrasound technology improves pigment intake. It can be clearly noted that the ultrasound almost doubles the pigment retention. Nevertheless, they do not indicate which ultrasound mechanism leads to this improvement.

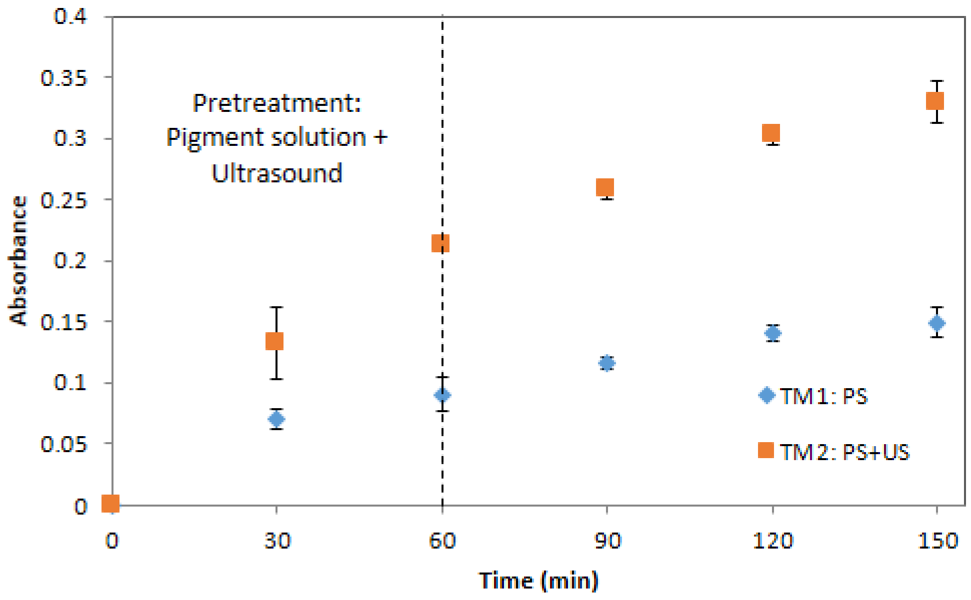

Figure 4.7 – Results of the treatments 1 and 2 the pigment solution transfer on melon cylinders (PS: pigment solution immersion; PS+US pigment solution immersion with ultrasound application). The dots are the average of the experimental values and the vertical bars are the standard deviation

Figure 4.8 shows treatments 3 (TM3), which consisted of pretreating the melon cylinders in water (as a control treatment) before they were immersed in the pigment solution, and 4 (TM4), which consisted of pretreating the melon cylinders in the ultrasonic bath before they were immersed in the pigment solution. They showed that pigment transfer was improved by applying the ultrasound as a pretreatment, demonstrating the formation of micro channels in the melon cylinders. These channels promoted the pigment influx by capillarity, increasing the total concentration of pigment in the melon cylinders. The micro-channel formation was caused by acoustic cavitation, which could cause cell disruption and/or matrix rupture inside the food, generating microscopic channels that reduce the internal resistance to the mass flow (CHEMAT; KHAN, 2011). In fact, this mechanism was demonstrated when ultrasound was applied as a pretreatment in melon before its dehydration (RODRIGUES; FERNANDES, 2007). Furthermore, it should be mentioned that the formation of micro channels in melon cylinders was probably faster than in the sorghum grains due to the softer matrix and higher water activity of the melon.

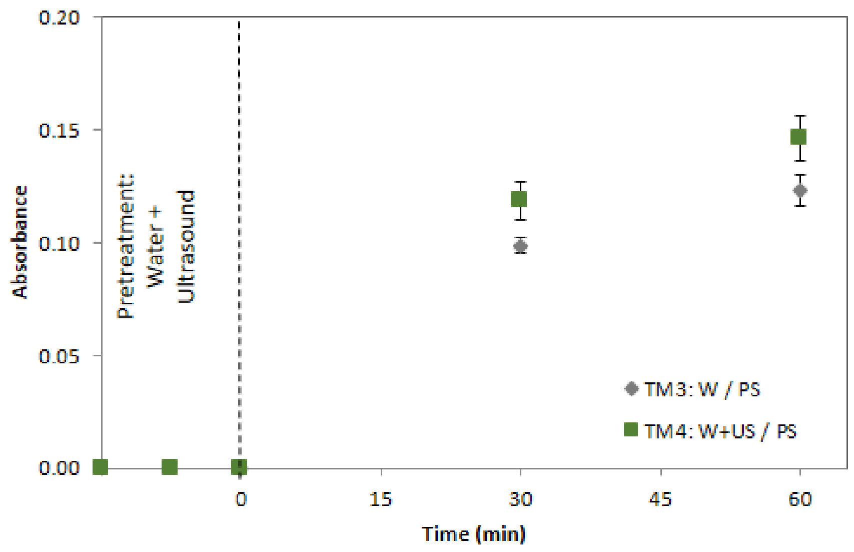

Figure 4.8 – Results of the treatments 3 and 4 for the pigment solution transfer on melon cylinders (W: water immersion; PS: pigment solution immersion; W+US water immersion with ultrasound application. The slash means that a pretreatment was used). The dots are the average of the experimental values and the vertical bars are the standard deviations

Figure 4.9 shows treatments 5 (TM5), which consisted of immersing the melon cylinders in the pigment solution without ultrasound, and 6 (TM6), which consisted of immersing the melon cylinders in the pigment solution with ultrasound, both using perforated melon cylinders. Consequently, these cylinders already contained many micro channels before contact with the pigment solution. It can be seen that pigment retention was higher even in the early stages of contact with the solution, where the micro-channel formation by the ultrasound is expected to be low in comparison with those previously generated by the needle. Therefore, this result demonstrated that the ultrasound enhancement of the mass transfer also occurs due to direct effects (inertial flow and “sponge effect”). Since the formation of micro-channel by cavitation needs time (due to the random distribution of cavitation until the formation of channels), these treatments were evaluated in only one hour in order to despise subsequent micro-channel formation and thus, evaluate only the direct effects. It can clearly be seen (Figure 4.9) that after 15 minutes, there was an improvement in pigment solution transfer, which means that the direct effect had taken place. Using ultrasound, the pigment flowed into the cylinders faster by the pre formed channels and all the natural cavities. Once they were full with the pigment solution, it was later transferred by diffusion, increasing the total concentration of the pigment inside the cylinders. The ultrasound waves also produced a rapid series of contractions and expansions ("sponge effect") in the melon cylinders, causing the pigment solution to flow through the preformed micro channels, enhancing the mass transfer by reducing internal resistance (MULET et al., 2003). It means that the direct effects of ultrasound are enhanced by the porosity of the medium.

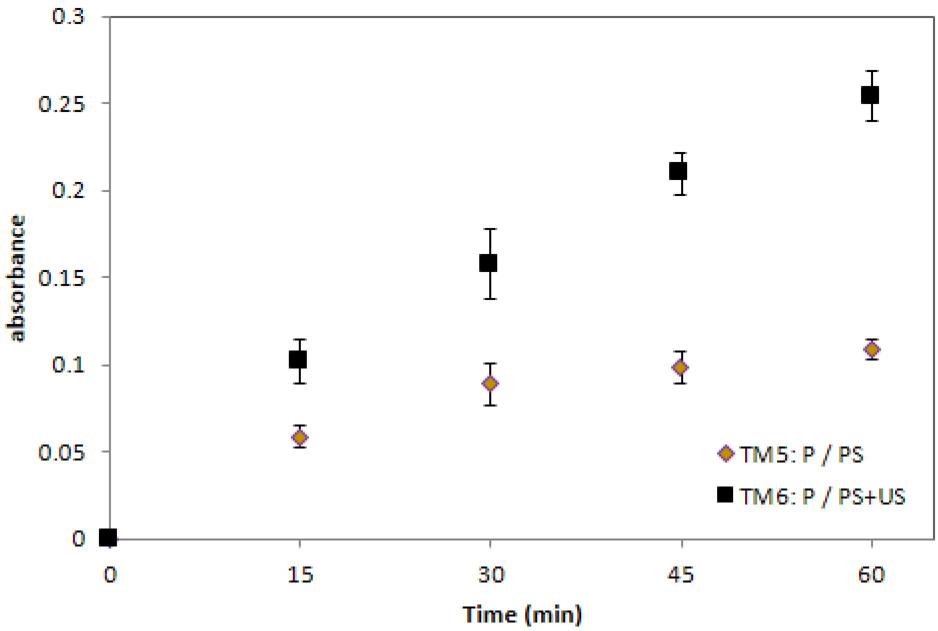

Figure 4.9 – Results of the treatments 5 and 6 for the pigment solution transfer on melon cylinders (P: needle perforation; PS: pigment solution immersion; PS+US pigment solution immersion with ultrasound application. The slash means that a pretreatment was used). The dots are the average of the experimental values and the vertical bars are the standard deviations

Finally, it is important to highlight that the obtained results can only be directly applied for the evaluated pigment influx into melon cylinders at this level of ultrasonic volumetric power. Each component that is transferred (mass transfer) through a food matrix has different behavior since they have different sizes, charge, molecular weight, etc. Therefore, the effect of the ultrasound technology could be different for different components. In addition, since the acoustic cavitation depends on the water vapor pressure, the ultrasound effect (especially the indirect effects) could change due to the water vapor pressure change with the presence of solutes. Further, different volumetric powers can change the relative importance of each mechanism during the ultrasonic processing. Despite this, the main qualitative finds of the present work can be generally interpreted.

4.3.3 Final Considerations

According to the results, the ultrasound-assisted processes could be optimized by taking the water activity and porosity of the food into count. If the aim is to take advantage of the indirect effects of ultrasound technology, for instance, in the drying process, it would be better to use the ultrasound technology as a pretreatment or in the first part of the process since the food has higher water activity. However, in the hydration process, it may be better to use the ultrasound technology after a certain time in the process when the food has a higher water activity. On the other hand, to take advantage of the direct effects of ultrasound technology, it would have to be used on porous food.

It should be mentioned that these results were obtained with a specific ultrasonic volumetric power and frequency (28 W/L; 40 kHz), similar to other works were the ultrasound technology was proven to enhance mass transfer processes in food (PATERO; AUGUSTO, 2015; ULLOA et al., 2015; YILDIRIM; ÖNER; BAYRAM, 2011). Different result could be obtained with different conditions of power and food products.

The direct effects (“sponge effect” and inertial flow) can be enhanced by the porosity and cavities of the food. The ultrasound waves generate the contraction and relaxation of the tissues causing the fluids be displaced since it acts as a pump. Therefore, spaces in the food are required to the flow of the fluid. The indirect effects (micro channels formation due to cavitation) can be affected by the structure. If the structure is very compact and rigid, the cavitation can take more time to generate cavities, or a higher ultrasound energy would be needed.

However, although the obtained results can only be directly applied for the two model cases here evaluated, the main qualitative finds of the present work can be generally interpreted.

In conclusion, this work can contribute to both academic knowledge and industrial application, since its results can help to optimize the different processes where mass transfer is involved, deciding at which point in the process it is better to use the ultrasound technology and reducing the cost and energy used.

4.4 Conclusions

This work demonstrated that the ultrasound mechanisms (indirect effect related to micro-channel formation by acoustic cavitation and the direct effects related to the inertial flow and the “sponge effect”) enhance the mass transfer in food. Further, those mechanisms can occur in food processing, and their importance is in function of the water activity in the food. Acoustic cavitation takes place more easily in food with higher water activity, resulting in micro-channel formation, while the direct ultrasound effects take place in both low and high water activity food. Moreover, the direct effects are enhanced by the porosity of the food and the micro channels formed. It was also demonstrated that cavitation forms cavities randomly. They are differentiated by their tortuosity and lack of connection with the external medium. Consequently, the micro channels need time to form well, resulting in an improvement in the mass transfer. As a conclusion, based on the results of this work, the application of ultrasound in food processing can be revised in order to maximize its effects, for example only applying it in some periods of the whole process.

Acknowledgments

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5 ULTRASOUND TECHNOLOGY ENHANCES THE HYDRATION OF CORN KERNELS WITHOUT AFFECTING THE STARCH PROPERTIES[1]

Abstract

This work studied the effect of the ultrasound technology on the hydration process of corn kernels, evaluating both the water uptake and the starch properties. For that, an ultrasound bath of 25 kHz of frequency and 41 W/L of volumetric power was used. Further, different treatments were performed in order to determine the mechanisms of enhancement of the hydration process (direct or indirect effects), by studying the hydration kinetics and the microstructure of the kernels. Finally, the rheological, thermal and structural properties of the starch extracted from the corn kernels (hydrated with and without ultrasound) were evaluated. Due to the particular behavior of the corn kernels during hydration, a two terms mathematical model was proposed to explain the process, which contains two simultaneous ways related with the different mechanisms of water influx. The ultrasound significantly improved the hydration process, increasing the water uptake and decreasing the process time ~35%. In contrast to other grains, it was proved that the enhancement of the process was only due to the direct effects (inertial flow and sponge effect) and not to the indirect effects (micro channels formation). Finally, it was demonstrated that the ultrasound technology did not change the starch properties. As a conclusion, it was proved that the corn kernels can be quickly hydrated using the ultrasound technology without modifying any property of their starch, being this highly desirable for the starch industry.

Keywords: Ultrasound; Hydration; Modeling; Corn kernels; Starch

5.1 Introduction

Corn is one of the most important crop in the world, being widely used in the food, chemical, pharmaceutical and agricultural industries, due to its high content of starch. Cornstarch, native, modified or cleaved, is used in food preparation, drug production, paper production, textile industry, petroleum refining, among others uses (BERTOLINI, 2010). Moreover, it is used as substrate for the ethanol production. The first unit operation during the corn processing is the hydration, which is carried out by water immersion, as it is necessary for wet milling the grains.

The hydration is a batch and lengthy process that may take up to 36 hours during corn processing (SINGH; ECKHOFF, 1996). Therefore, the optimization of the

[1] This Chapter is currently under review:
MIANO, A.C.; IBARZ, A.; AUGUSTO, P.E.D. 2015. Ultrasound technology enhances the hydration of corn kernels without affecting the starch properties.

hydration process is very desirable for the starch industry, being important studying technologies to enhance this process. The ultrasound technology seems to be a promising option.

The ultrasound technology has been widely studied as an alternative to improve the food processing, such as on defoaming, freezing, extraction, emulsification, hydration, drying, (AWAD et al., 2012) and germination (MIANO, et al., 2015). The application of ultrasound had good results for the hydration process of chickpeas (YILDIRIM; ÖNER; BAYRAM, 2013), navy beans (GHAFOOR et al., 2014), sorghum grains (PATERO; AUGUSTO, 2015) and common beans (ULLOA et al., 2015), reducing the process time and increasing the equilibrium moisture. However, the hydration process of a grain with high economic importance, such as corn, has not been studied yet, as well as the impact of this process on the starch properties. It should be a very important evaluation from an industrial point of view.

Furthermore, from a scientific point of view, much more than prove the effect of the ultrasound technology, it should be important to demonstrate the mechanisms that allow the process improvement. As described by Miano et al. (2015), most of the published works only mention all the possible effects of the ultrasound technology on the mass transfer processes, although each specific process and condition has its own mechanisms (direct and indirect effects) taking place. Therefore, the importance of evaluating the exact mechanisms that take place during the corn hydration is desirable.

Finally, it is highly desirable to enhance the hydration process of grain without impairing its quality, in special its starch properties. In consequence, this work studied and described the effect of the ultrasound technology on the hydration process of corn kernels, verifying the possible effects on the starch properties by comparing the pasting properties, thermal properties and microstructure.

5.2 Materials and Methods

5.2.1 Hydration process

During the experiments, an ultrasonic bath with 25 kHz of frequency and 41 W/L of volumetric power (Q13/25, Ultronique Brazil; determined following the method described by Tiwari et al. (2008)) was used. This bath has its piezoelectric elements arranged below the tub. It generates the mechanical waves that are transmitted through the water, addressing the product.

Corn kernels (*Zea mays* var. *amylacea*; gently provided by Ingredion Brazil) with 12.55±0.55 % d.b. (g water / 100 g of dry matter) of moisture content were used. For the hydration process, 15 g of pre-selected kernels were soaked in 4 L of distilled water at 25°C with and without using ultrasound. During the hydration process, the samples were periodically drained, superficially dried and its moisture content was obtained by mass balance. The sampling was carried out every 20 min for the first hour and every 30 minutes for the later hours, until constant mass. The hydration process was performed at constant temperature and in triplicate.

5.2.2 Hydration mechanisms and effect of ultrasound technology

The ultrasound enhances the mass transfer due to two possible mechanisms: direct and indirect effects produced by the alternative expansion and rarefaction of the sound wave. The direct effects are related to the inertial flow (the fluid inside the food is pumped because of the difference of pressure caused by the wave traveling) and the so-called “sponge” effect (when the cells or the food matrix is compared to a sponge squeezed and released repeatedly). The indirect effects are related to the cell disruption and micro channels formation due to acoustic cavitation (According to the results of the CHAPTER 4). Therefore, experiments were carried out in order to evaluate the mechanisms that take place during the hydration of corn kernels with the ultrasound technology.

To verify if the micro channels were formed during the process (the so-called indirect effects), the kernels were pretreated with ultrasound, for then being conventional hydrated. One layer of corn kernels was vacuum packed in order to treat the kernels with ultrasound without hydration. This pack was placed at the bottom of the water bath to receive better the ultrasound waves. After 3 h and 5 h of pretreatment (the conditions were determined after pretests and taking into account the time magnitudes to hydrate the grains), the kernels were unpacked and conventionally hydrated without ultrasound application at 25 °C. Corn kernels with high moisture content (40 g water / 100 g d.b; water activity of 0.988 ± 0.005) were also evaluated, since in CHAPTER 4 was demonstrated that it is possible necessary a grain with higher moisture content (higher water activity) to the cavitation take place. To obtain grains with the higher moisture content, the corn kernels were previously hydrated for 6 hour and storage for one week at 5 °C in order to homogenize the moisture in the tissues.

To verify if the direct effects (“sponge effect” and inertial flow) took place during the process, the kernels were hydrated with different treatments using or not the ultrasound technology. The first treatment (US + N) consisted of hydrating the kernels using ultrasound for the three first hour, for then hydrated them without ultrasound. The second treatment (N + US + N) consisted of hydrating the kernels without ultrasound for the first three hours. The next three hours they were hydrated with ultrasound, and finally they were hydrated without ultrasound (the conditions were determined after pretests and taking into account the time magnitudes to hydrate the grains).

In addition, fingernail polish was used as sealant to cover the pericarp or the tip cap (RAMOS et al., 2004) in order to determine the effect of ultrasound on the hydration rate of these structures.

Finally, the microstructure of the corn kernels was analyzed by SEM analysis and X-ray. For SEM, the samples were cut in order to see the different tissues (pericarp, endosperm and tip cap) and dehydrated using silica gel for 3 days. Them, they were sputtered with a 30 nm gold layer. Finally, the samples were observed in a scanning electronic microscope operated at an acceleration voltage of 15 kV (LEO 435 VP, Leo Electron Microscopy Ltd., Cambridge, England). SEM was performed for corn kernels hydrated with and without ultrasound. For X-ray analysis, the kernels were X-rayed using a model MX-20 DC-12 digital Faxitron X-ray, exposing them to the radiation at 20 kV for 10 s. The grains were X-rayed at different positions in order to evaluate the internal structure.

5.2.3 Mathematic modeling of the hydration process

The corn kernels hydration kinetics was modeled using different equations, which describe a downward concave shape (DCS) behavior: Peleg model (PELEG, 1988), Page model (PAGE, 1949), First order kinetics model (LEWIS, 1921), Ibarz-González-Barbosa-Cánovas model (IBARZ; GONZÁLEZ; BARBOSA-CÁNOVAS, 2004) and the proposed model in this work (Table 5.1). The proposed model is an equation with two terms, similarly to that used to explain the drying process (VERMA et al., 1985).

For that, the kernels moisture content at dry basis (M; g water / 100 g of dry matter) versus time (min) of the hydration process was evaluated for each initial moisture. The data were fitted to the mathematical models with a confidence level of 95% using the Levenberg-Marquardt algorithm in Statistica 12.0 (StatSoft, USA) software. The goodness of the models fitting was evaluated by the coefficient of determination (R^2) of the regression value, the root-mean-square deviation values (RMSD, eq. (5.1)), the normalized RMSD (NRMSD, eq. (5.2)).

$$RMSD = \sqrt{\frac{\sum_{i=1}^{n}(M_{experimental} - M_{model})^2}{n}} \qquad (5.1)$$

$$NRMSD = 100 \cdot \frac{RMSD}{(M_{experimental})_{maximun} - (M_{experimental})_{minimun}} \qquad (5.2)$$

5.2.4 Starch properties

The starch of the corn kernels (hydrated with and without ultrasound) was extracted as follow: The corn kernels were soaked in a sodium methabisulfite solution (0.1 % w/v) for 72 h at 60 °C, followed by manually removing of the pericarp and germ with a spatula. Then, the endosperms were wet milled (with 3 times in weight of distilled water) using a blender for 20 s and sieved (60 and 325 mesh). The supernatant was washed two times with distilled water and sieved again. The filtrate was centrifuged at 3200 g for 5 min, for them separating the starch from the rest of the components (water, proteins and lipids). Finally, the starch was dried at 35 °C for 6 h in a flat tray and was softly milled using a mortar and pestle.

In order to evaluate if the starch of the hydrated corn kernels was affected by ultrasound, the following evaluation was performed**.**

The pasting properties (rheological) were evaluated in a Rapid Visco Analyzer (RVA-S4A; Newport Scientific, Warriewood, NSW, Australia) using 3 g of sample (14% of moisture) in 25 g of water. The suspension was first held at 50 °C for 1 min and then heated to 95 °C at a rate of 6 $°C \cdot min^{-1}$. The sample was then held at 95 °C for 5 min, followed by cooling to 50 °C at a rate of 6 °C·min^{-1}, and finally holding it at 50 °C for 2 min.

The thermal properties of the starch were evaluated in a differential scanning calorimeter (DSC-60 Shimadzu, Japan). A corresponding sample of 3 mg of dry starch was place in an aluminum pan with 7 µL of deionized water. The samples in the hermetically sealed pans were equilibrated at room temperature for 1 h before measurement. The scanning temperature was from 30°C to 95 °C and the heating rate was 10 °C·min^{-1}. An empty pan was used as reference.

To obtain the X-ray diffraction profiles, the starch moisture was balanced in a desiccator containing saturated $BaCl_2$ solution (25 °C, a_w = 0.900) for 10 days. The patterns of X-ray diffraction were determined in a X-ray diffractometer (Miniflex II, Rigaku, Tokyo, Japan) using copper radiation, at a scanning speed of 2° per min, angle 2 (2θ) ranging from 4° to 50°, 40 kV, and 40 mA. The relative crystallinity of starch was quantitatively determined following the method proposed by Nara and Komiya (1983) and using the Origin 7.5 software (Microcal Inc., Northampton, MA, USA). The data were smoothed with the Adjacent Averaging tool and plotted in graphs between 2 angles (2θ) ranging from 4° to 30°.

The structure of the starch was analyzed using Scanning Electronic Microscopy (SEM). A thin layer of dry starch (which was obtained using a brush) was sputtered with a 30 nm gold layer and observed in a scanning electronic microscope operated at an acceleration voltage of 20 kV (LEO 435 VP, Leo Electron Microscopy Ltd., Cambridge, England).

5.3 Results and Discussion

5.3.1 Hydration process description

The hydration of the corn kernels showed a downward concave shape (DCS) behavior (Figure 5.1), as expected (FERNÁNDEZ-MUÑOZ et al., 2011; MARQUES; JORGE; JORGE, 2014; RAMOS et al., 2004; VERMA; PRASAD, 1999). This behavior is described by a higher hydration rate at the beginning of the process, which is continuously reduced during the process. Particularly, and differently from other grains, the corn kernel was characterized by a very fast hydration in the first part of the process until a certain time when the hydration process starts to be slower. In fact, it seems that the corn kernels hydrate in two steps. Therefore, it is very important to describe this phenomenon properly (Figure 5.1).

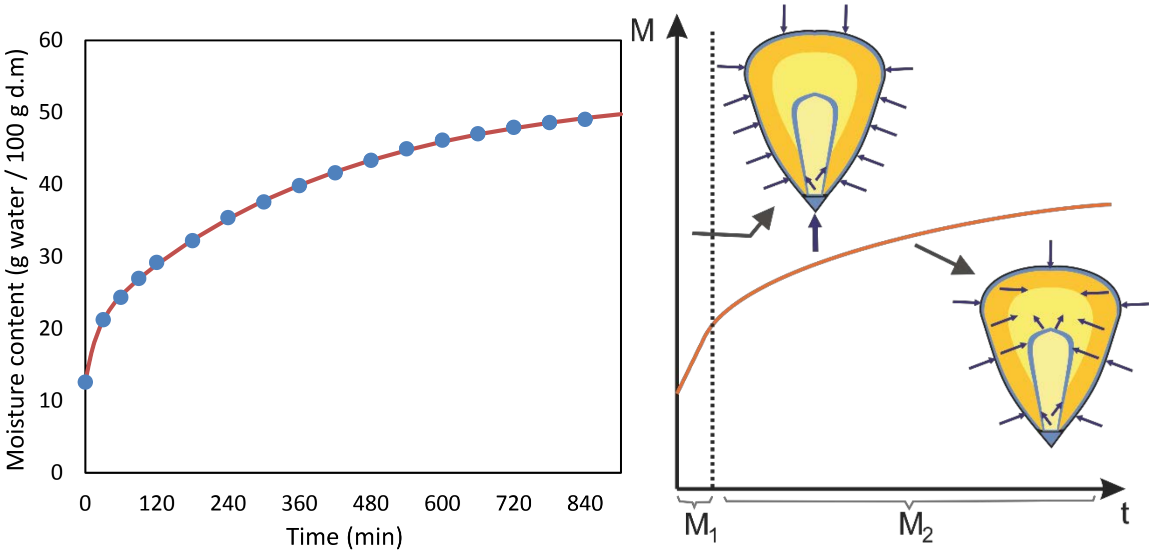

Figure 5.1 – Left: Hydration kinetics of corn kernels. The dots are the experimental values and the line represents the model prediction (eq. (5.11)). Right: Hydration process description (First step M_1 and second step M_2); the arrows indicate the water flow into the grain

The equilibrium moisture (M_∞) is reached in approximately 14 h of soaking, being thus a very slow process in comparison with other grains. Further, the quantity of absorbed water is approximately 4.5 times the initial moisture content, being similar to other starchy grains, like ~3 times for wheat (IGATHINATHANE; CHATTOPADHYAY, 1997), ~3.5 for rice (BELLO; TOLABA; SUAREZ, 2004) and ~3.3 times for sorghum (PATERO; AUGUSTO, 2015); and very different to legumes (higher protein content), for instance, ~21 times for soy bean (SOPADE; OBEKPA, 1990), ~30 times for chickpeas (GOWEN et al., 2007), ~11 times for Andean lupin (MIANO; GARCÍA; AUGUSTO, 2015) and ~9 for Adzuki beans (MIANO; AUGUSTO, 2015). It confirms that the composition affects the water holding capacity of the grains.

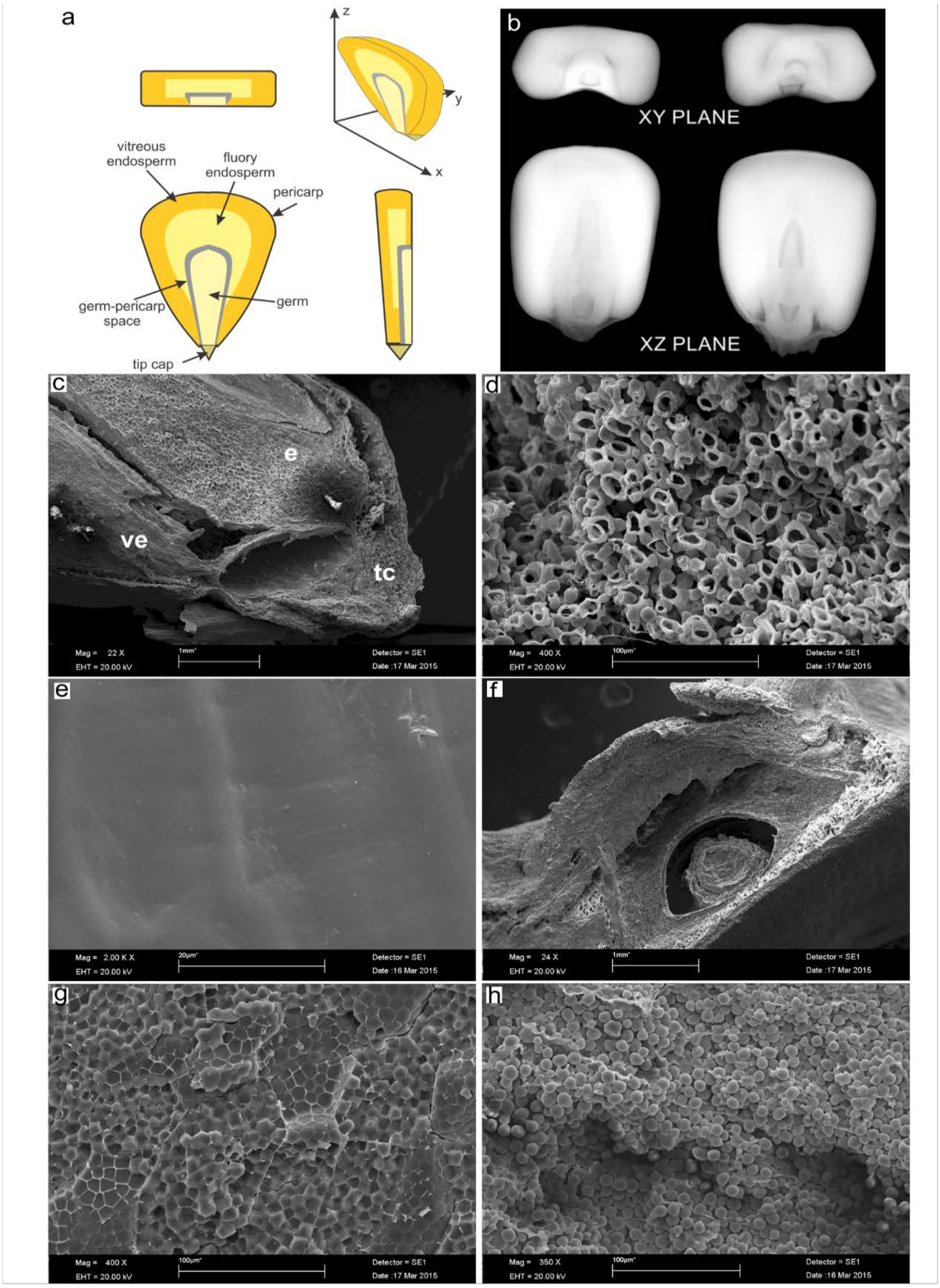

Figure 5.2 – Structure of corn grain. a. General morphology of the grain. b. Radiography of the grain. c. SEM of XZ plane section: tc, tip cap; e, germ; ve, vitreous endosperm. d. SEM Tip cap. e. SEM Pericarp surface. f. SEM XY plane section (germ region). g. SEM Vitreous endosperm. h. SEM Floury endosperm. SEM, 20 kV; the magnifications are shown in the figures

In the corn kernels, the water enters by both the tip cap and the pericarp (Figure 5.1). Since the tip cap is formed by tube cells, the water enters by capillarity; further, the flux of water (mass of water transferred per unit area and time) is larger than the flux on the pericarp, which lets the water enters by diffusion (RAMOS et al., 2004). The tubes cells of the tip cap had ~11 µm of diameter (Figure 5.2-d), letting the water enters by capillarity. However, since the pericarp area is much larger than the tip cap area, most of the hydration occurs through the pericarp (RAMOS et al., 2004; RUAN; LITCHFIELD; ECKHOFF, 1992). In addition, there is a space between the endosperm and germ (Figure 5.2), which is initially “empty” and then it is filled with water due to capillary flow from the tip cap. This explains the very fast hydration behavior in the first step of the hydration process (M_1). In the second step (M_2), the germ and endosperm are probably hydrated from the bulk water, the film of water between the endosperm and pericarp and the water presented in the space between the endosperm and the germ (Figure 5.1). This process is slow in comparison with the first step, probably due to the compactness of the endosperm, especially in the vitreous region (Figure 5.2-g).

Due to this hydration behavior (very fast hydration rate at the beginning of the process and slower hydration rate at the rest of the process), many common mathematical models do not successfully fit the hydration of corn kernels. Therefore, a suitable model had to be find.

5.3.2 Mathematical modeling of the hydration process

The corn kernels hydration kinetics data (25 °C) were plotted and modeled using the most used hydration kinetics mathematical models (Table 5.1). However, many of them did not fit well the experimental data (Figure 5.3), even presenting a suitable statistical fit. Moreover, some mathematical models have parameters that are difficult to explain in a physical way. Therefore, a new model was proposed and evaluated here.

Table 5.1 – Mathematical models used to describe the hydration process of corn kernels

Model Name	General form	Parameters mean values	M_∞ (%$_{d.b.}$)	R^2	RMSD (%$_{d.b.}$)	NRSD (%)
Peleg	$M = M_o + \frac{t}{k_1 + k_2 \cdot t}$	k_1 = 4.656 min·%d.b^{-1}.; k_2 = 0.224 %d.b^{-1}	57.3	0.988	1.12	3.07
Page	$M = M_\infty + (M_o - M_\infty) \cdot e^{-k_3 \cdot t^{k_4}}$	k_3 = 0.022 min^{-k4}; k_4 = 0.586	67.0	0.999	0.31	0.84
First order kinetic	$M = M_\infty + (M_o - M_\infty) \cdot e^{-k_5 \cdot t}$	k_5 = 0.0046 min^{-1}	48.3	0.974	1.69	4.66
Ibarz-González-Barbosa-Cánovas	$M = \left(\frac{k_6}{k_7}\right) - \left(\frac{k_6}{k_7} - M_o\right) \cdot e^{-k_7 \cdot t}$	k_6 = 0.224 min^{-1}·%d.b; k_7 = 0.0046 min^{-1}	48.3	0.981	1.69	4.66
Proposted model	$M = M_\infty + (M_o - M_\infty) \cdot (p \cdot e^{-k_8 \cdot t} + (1-p) \cdot e^{-k_9 \cdot t})$	p = 0.191; k_8 =0.05312 min^{-1}; k_9 = 0.00252 min^{-1}	53.2	0.999	0.15	0.42

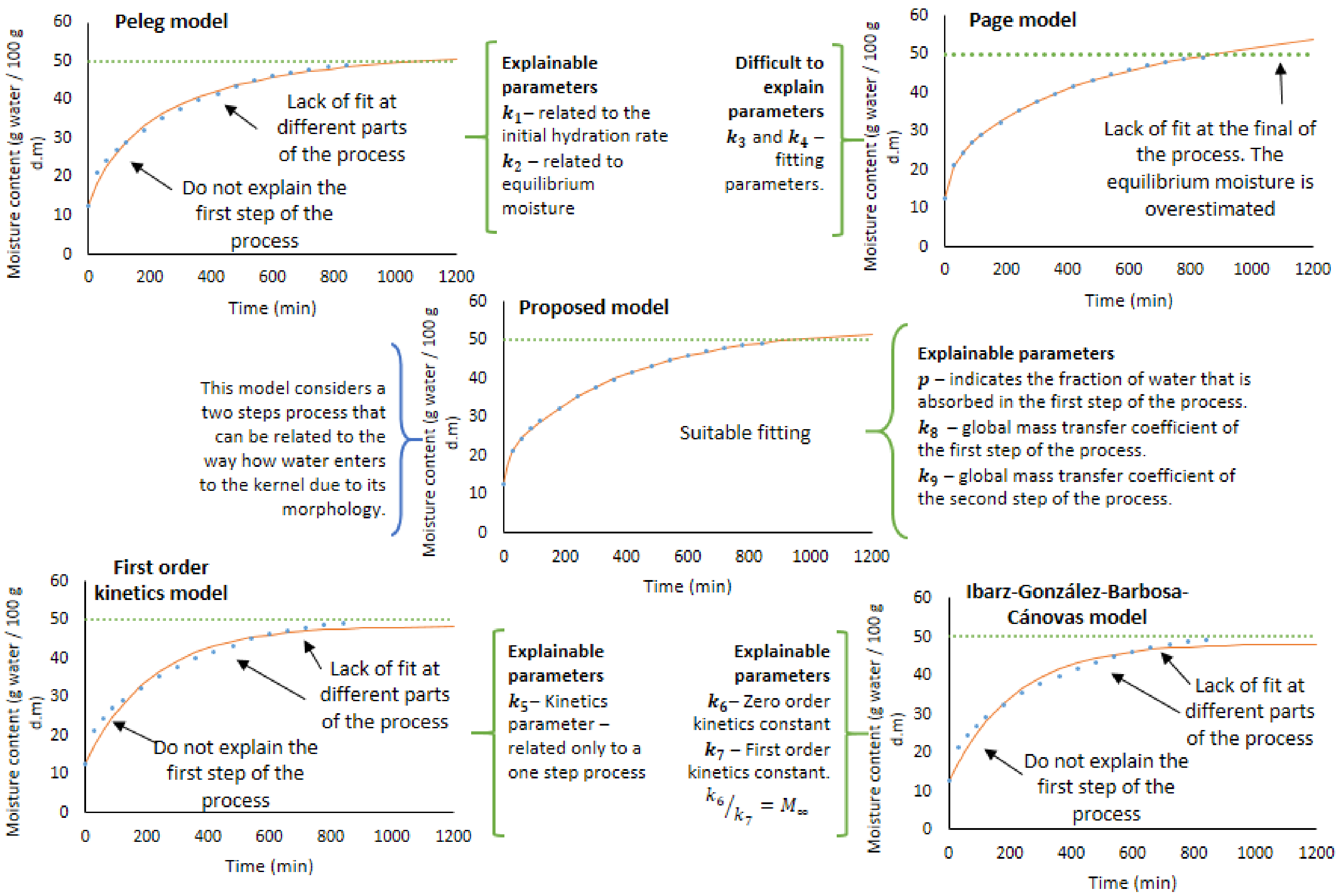

Figure 5.3 – Advantages and disadvantages of the different mathematical models (from Table 5.1) using to describe the corn kernels hydration process. The dots are the experimental values and the continuous lines are the model prediction

The Peleg model (PELEG, 1988), has been widely used to explain the hydration process of several grains. It is, without doubt, the most widely used in the literature. This model has two explainable parameters, one of them is related to the hydration absorption rate (k_1) and the other is related to the equilibrium moisture reached during the process (k_2). For corn kernels, it has a good statistical fitting (Figure 5.3). However, this fitting was not enough to explain the corn kernel hydration since the model had a bad fitting at the beginning of the process and it did not appropriately predict the equilibrium moisture. It can be clearly seen in Figure 5.3 where it is highlighted that a good statistical fitting does not necessarily represent a good description of the phenomena.

The Page model (PAGE, 1949) is more used for describing the drying process (ERBAY; ICIER, 2010); nevertheless, it can be also used for describing the hydration process since it is an exponential equation. This model had better fitting than the Peleg model (Figure 5.3). However, it has one parameter (k_4) difficult to explain, without physical explanation. Further, the predicted equilibrium moisture was overestimated.

The First order kinetics model (LEWIS, 1921) is also more used for describing the drying process (ERBAY; ICIER, 2010), although it can also be used to describe the hydration process. This model statistically fitted well the data (Figure 5.3) and it has only one parameter (kinetics constant). Nevertheless, this model did not fit the beginning of the process.

The Ibarz-González-Barbosa-Cánovas model was also evaluated (ERBAY; ICIER, 2010; IBARZ et al., 2004). This model is similar to the first order kinetics model and it has two explainable parameters. As the first order kinetics model, it had a good statistical fitting on the corn kernels hydration data. Nevertheless, it did not also fit the first part of the process.

The hydration process of the corn kernel takes place in two steps due to the morphology of the grain as described above. In addition, the water enters by diffusion and capillarity because of their complex structure with different tissues and cavities. Both mechanisms take place simultaneously; however, the capillarity phenomenon is probably predominant in the first step of the hydration process due to the porosity of the tip cap and the “empty spaces” in the grain, and probably the diffusion phenomenon in the second step of the process due to the compactness of the endosperm and germ. Therefore, it suggests that the mechanisms of water influx into the corn grains during the hydration process are complex, being necessary the evaluation of further models that can explain the water flow route.

It is interesting to mention that a composed model that combines two Peleg equations in series was used to describe the wheat grains hydration (PAQUET-DURAND et al., 2015). This model considered the first term for the hydration of the bran layer, and the second term for the hydration of the endosperm. Therefore, they explained the model by the hydration of each tissue separately. In contrast, it was shown that the corn kernels hydration takes place by two steps, with the hydration of the tissues simultaneously. As a result, the model proposed by those authors (PAQUET-DURAND et al., 2015) was not evaluated, being proposed the following one.

5.3.3 Description of the proposed model

Since the corn kernels hydration is carried out in two steps (Figure 5.1), it is proposed a two-term equation to describe this behavior (Table 5.1, Figure 5.3, eq. (5.11)). This equation is originated by the following reasoning.

The absorbed water as function of time is represented by eq. (5.3), where k is the global coefficient of mass transfer, related to the diffusion and capillary mechanisms in combination. The value of $(M_\infty - M)$ is the driving force:

$$\frac{dM}{dt} = k \cdot (M_\infty - M) \tag{5.3}$$

This equation can be integrated with the appropriated boundary limit (eq. (5.4)), thus obtaining eq. (5.5) (which can be rearranged as eq. (5.6)).

$$\int_{M_0}^{M} \frac{dM}{(M_\infty - M)} = \int_0^t k \cdot dt \tag{5.4}$$

$$\frac{M_\infty - M}{M_\infty - M_0} = \exp(-k \cdot t) \tag{5.5}$$

$$M = M_\infty - (M_\infty - M_0) \cdot \exp(-k \cdot t) \tag{5.6}$$

The hydration process of corn kernels has two steps. Thus, the total water absorbed (M) can be represented by eq. (5.7):

$$M = M_1 + M_2 \tag{5.7}$$

In addition, the water fraction that is absorbed in the first step can be represented as “p”. Consequently, the water absorbed in the second step will be “1 - p”, thus obtaining eq. (5.8) and eq. (5.9).

$$p = \frac{M_1}{M} \tag{5.8}$$

$$1 - p = \frac{M_2}{M} \tag{5.9}$$

Replacing eq. (5.8) and eq. (5.9) into eq. (5.7), eq. (5.10) is obtained:

$$M = p \cdot M + (1 - p) \cdot M \tag{5.10}$$

Finally, replacing eq. (5.6) into eq. (5.10), the proposed model is obtained (eq. (5.11)), being the parameters k_8 and k_9 the global coefficients of mass transfer of each step of the hydration process.

$$M = M_\infty - (M_\infty - M_0) \cdot (p \cdot \exp(-k_8 \cdot t) + (1 - p) \cdot \exp(-k_9 \cdot t)) \tag{5.11}$$

This equation has a suitable fitting of the experimental data (R^2=0.999; RMSD=0.15 % d.b.; NRSD=0.42 %; Table 5.1; Figure 5.1 and Figure 5.3). Furthermore, and most important, it explains the process estimating well the equilibrium moisture and having explainable parameters.

This model has four parameters: the equilibrium moisture content (M_∞); the parameter “p” which means the fraction of water that is absorbed by the kernel in the first step of the process; and the two global mass transfer parameters (k_8 and k_9) (Table 5.1 and Figure 5.3).

The p value was 0.191 (Table 5.1). It means that approximately 19 % of the total absorbed water is absorbed in the first step (where the predominant mechanism is the capillarity) and the other 81 % is absorbed in the second step (where the predominant mechanism is the diffusion). In fact, this can be also graphically confirmed in the Figure 5.1.

By using the parameter “p”, the first step duration can be estimated. The value of the maximum absorbed water ($M_\infty - M_o$) was 44.62 g water / 100 g d.b. The 19.1 % of this absorbed water was 8.52 g water / 100 g db. Knowing that the initial moisture of the corn kernels was 12.55 g water / 100 g d.b, then, during the first step of the process, the kernels would have reached 21.07 g water / 100 g d.b of moisture content. In consequent, the necessary time to reach that moisture was approximately 29.5 min (Figure 5.1).

The value of k_8 is ~20 times higher than the k_9 value, reinforcing that the rate of water absorption during the first step of the hydration process is much higher than the rest of the process. It is interesting to observe that, although the first step has a very high water absorption rate, it has a short duration (~30 min, comparing with the ~14 h of hydration).

Therefore, the proposed model successfully explained the hydration of the corn kernel following its morphology and having explainable parameters, which is very desirable.

5.3.4 Effect of the ultrasound technology on the corn kernels hydration process

Figure 5.4 shows that the ultrasound technology highly enhanced the hydration process of the corn kernels. This technology reduced significantly the process time approximately 35 %, which represent almost 5 hours of reduction time. Since the hydration process is a discontinuous and time consuming process, this reduction of time is very desirable for the industries, improving the process efficiency.

Both the hydration rate and the equilibrium moisture content were increased. These desirable results were also reported for chickpeas (YILDIRIM et al., 2013), navy beans (GHAFOOR et al., 2014), sorghum grains (PATERO; AUGUSTO, 2015) and common beans (ULLOA et al., 2015). The principal attributed mechanisms of enhancements by these works were the indirect effect (micro channels formation by the acoustic cavitation) and the direct effects (inertial flow and sponge effect). The existence of both was demonstrated for sorghum grains (CHAPTER 4), although the existence or absence, as well as the relative importance of each one, was demonstrated to be function of the food water activity. Further, as each grain has different behavior due to its morphology and composition, it is highlighted the need for further evaluations.

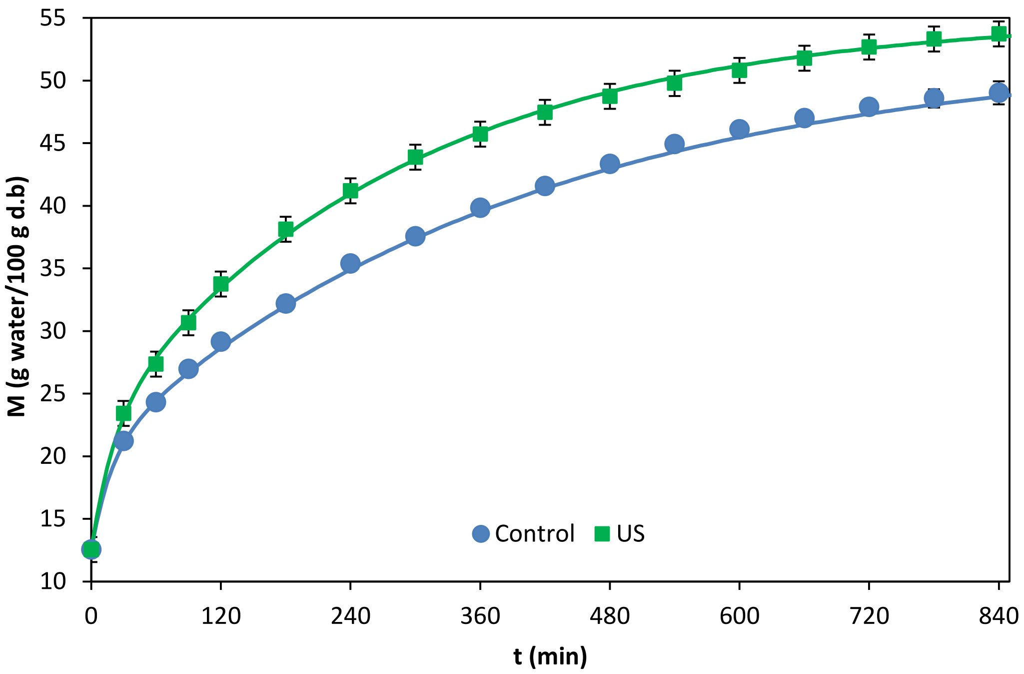

Figure 5.4 – Effect of ultrasound on the hydration kinetics of corn kernels. The dots are the experimental values; the vertical bars are the standard deviation and the lines are the proposed model (eq. (5.11)) estimation

Therefore, different especial treatments were performed in order to evaluate which mechanism improved the hydration of corn kernels by the ultrasound technology (Figure 5.5).

When the corn kernels were hydrated with ultrasound for periods of 3 hours, they showed an enhancement only during that time (treatment US+N and N+US+N, Figure 5.5-a). Nevertheless, when they were conventional hydrated again, the hydration rate decayed, reaching the hydration rate of the conventional hydrated corn kernels. It means that the corn kernels hydration process needs to be assisted by ultrasound in order to be improved, demonstrating that the direct effects took place and that there are not indirect effects (micro channels formation).

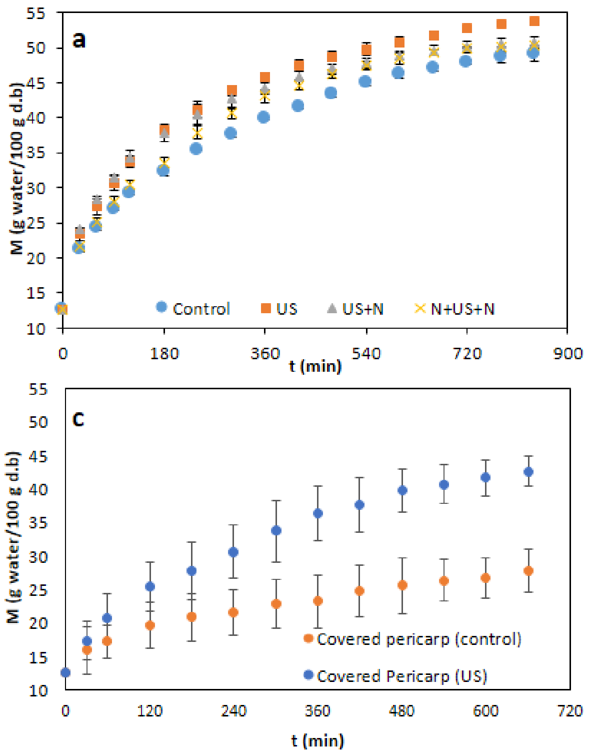

Figure 5.5 – Evaluating the mechanism of water absorption improvement due to the ultrasound technology: a. Treatments to evaluate the direct effects. b. Treatments to evaluate the indirect effects (micro channels formation). c. Comparison between the hydration kinetics without and with ultrasound through the tip cap. d. Comparison between the hydration kinetics without and with ultrasound through the pericarp. The dots are the experimental values and the vertical bars are the standard deviation

For instance, the pressure differences in the water and inside the kernels due to the wave propagation and the “sponge effect” could cause the water pumping inside the grain (the so-called inertial flow), accelerating the hydration process. It was demonstrated that for sorghum grains (According to the results of the CHAPTER 4) with low water activity, the micro channel were not formed by ultrasound technology, because the low water vapor pressure avoids the acoustic cavitation.

The vacuum-packed corn kernels with high water activity (water activity of 0.988 ± 0.005; moisture of 40 g water / 100 g d.b), which were treated with ultrasound (at different times), were then conventional hydrated, obtaining any improvement on the hydration process (treatment 3 h and 5 h, Figure 5.5-b). It means that there was not formation of micro channel, even at a high water activity.

The absence of micro channels formation on corn kernels can thus be related with its microstructure.

The micro channels formation due to the ultrasound technology was demonstrated for sorghum grains (According to the results of the CHAPTER 4) when they had high water activity (0.985 ± 0.002); however, for corn kernels, they were not formed. It could be due to the higher compactness of the vitreous endosperm in this grain (Figure 5.2). In corn, the endosperm cells are packed with starch granules embedded in a continuous matrix of amorphous proteins (KULP, 2000), which probable avoid the formation of micro channels by cavitation (at least at the present power conditions of 41 W/L). In fact, Figure 5.6 shows that any micro channels were formed in the different tissues of the corn kernel (pericarp, tip cap and endosperm). Therefore, the enhancement of the hydration process for corn kernels could be only due to the direct effects. Furthermore, due to the rigid structure of corn kernel, it is probably that the enhancement is preferably due to the inertial flow, as the “sponge effect” needs a series of contraction and expansions of the existenting channels to take place.

Figure 5.5-c and Figure 5.5-d show that the ultrasound enhances the water flow throughout both the pericarp and the tip cap.

When the pericarp was sealed (Figure 5.5-c), the hydration was carried out only by the tip cap. The ultrasound improved the hydration process by the tip cap. The tip cap is very porous, with structures similar to tubes (Figure 5.2 and Figure 5.6). Therefore, the water is probably pumped through these “tubes” because of the wave traveling.

When the tip cap was sealed (Figure 5.5-d), the hydration was carried out only by the pericarp. The ultrasound also improved the hydration rate in this case, being the improvement very significant since the hydration kinetics of this covered kernels was the same to the uncovered kernels hydration kinetics, both with ultrasound (i.e., the mass transfer improvement due to the ultrasound was most important than the suppression of mass transfer through the tip cap).

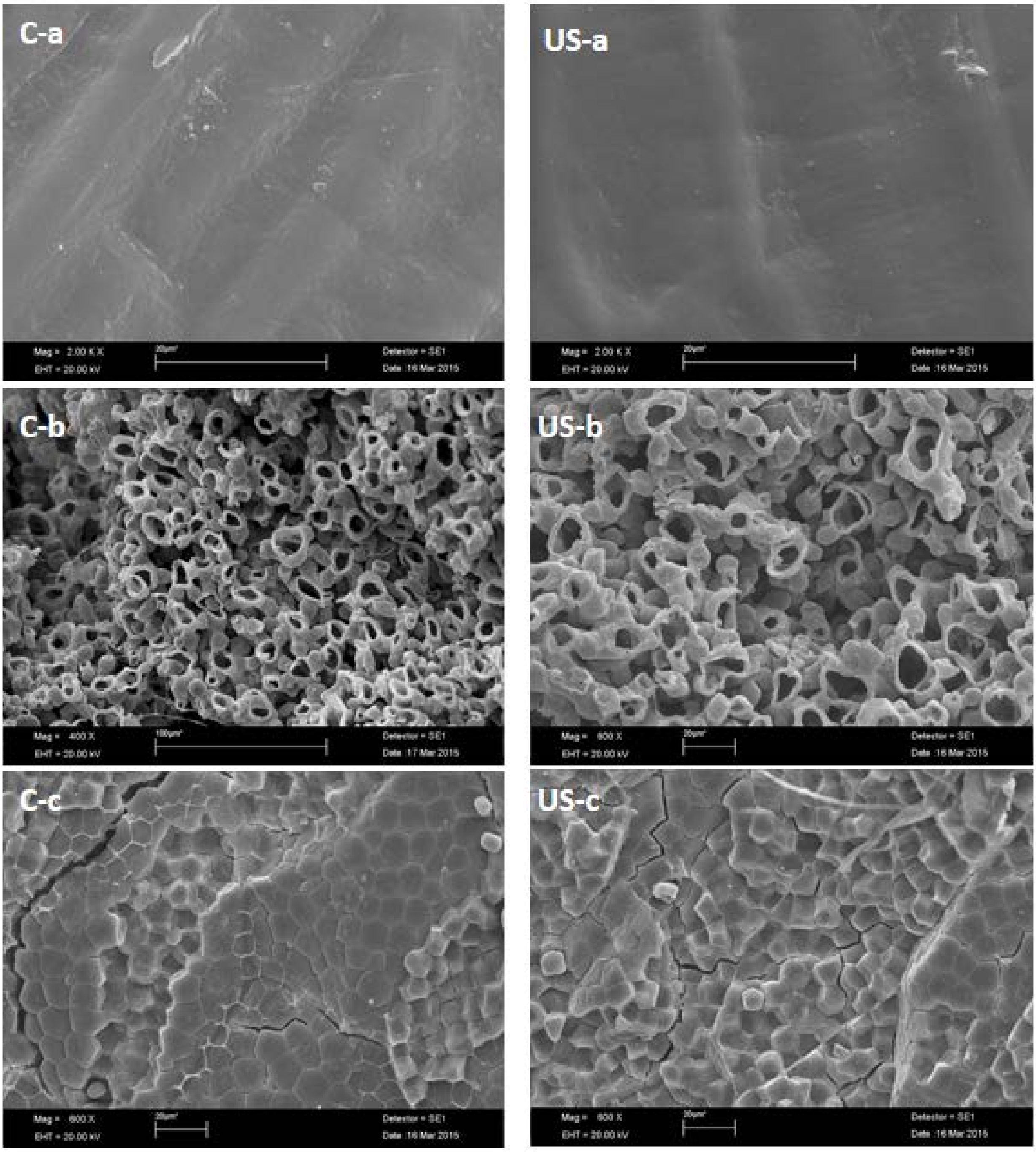

Figure 5.6 – Effect of ultrasound on corn kernels microstructure (SEM, 20 kV; the magnifications are shown in the figures). The captions C and US indicate the treatments without and with ultrasound respectively. The lowercase letters a, b, c indicates the observed tissue: pericarp, tip cap and endosperm respectively

The microstructure analysis (Figure 5.6) shows that, as expected due to the hydration results (Figure 5.5), there was not any structural change on the kernel tissues. In addition, it demonstrates any micro channel formation in the seed coat (pericarp), tip cap and endosperm. It can also be seen the compactness and the lack of intercellular spaces of the endosperm, and the lack of porosity of the pericarp, indicating that the water transfer in these tissues is mainly by diffusion. In contrast, the porosity of the tip cap permits the water entrance by capillarity.

Finally, Figure 5.7 shows the effect of ultrasound on the proposed model parameters.

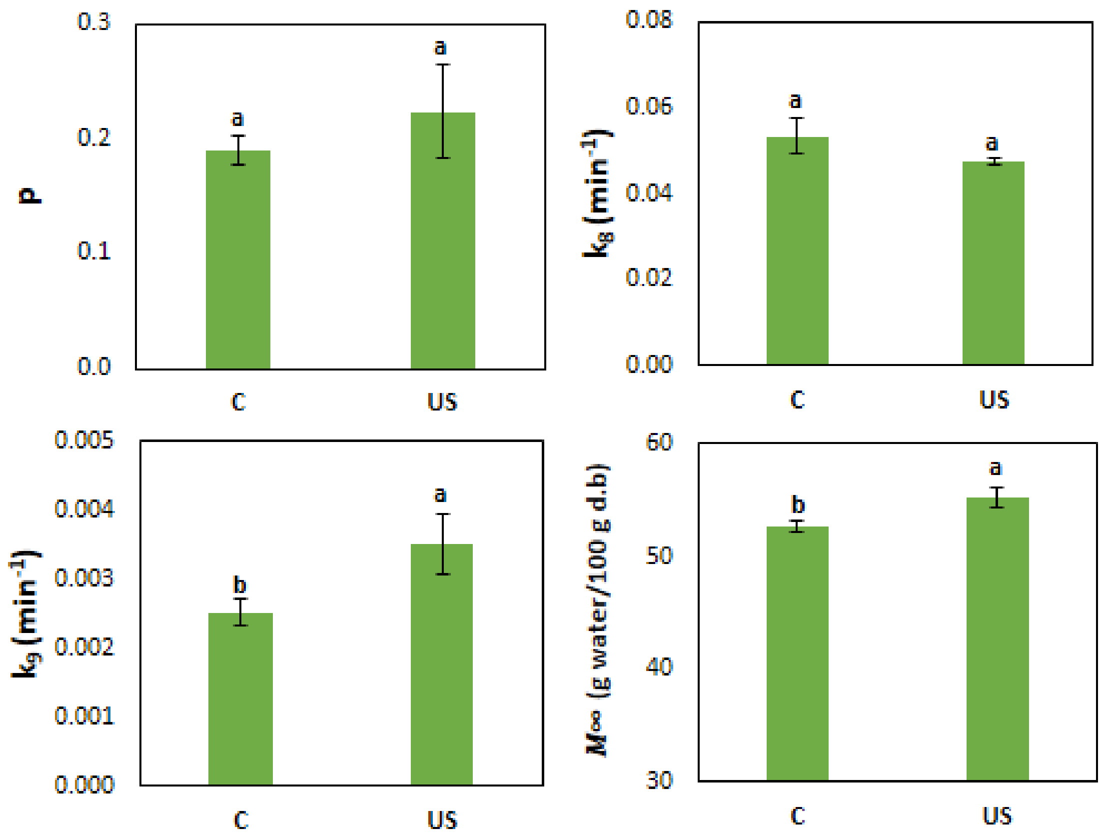

Figure 5.7 – Effect of ultrasound on the proposed model parameters (C: without ultrasound; US: with ultrasound) (eq. (5.11)). The letters above the bars represent the mean comparison of Tukey test ($p<0.05$)

The equilibrium moisture (M_∞) significantly increased 5 %. Since it was demonstrated that micro channels were not formed in the corn kernels, the explanation of this improvement can be due to the ultrasound keeps the porous and internal cavities unobstructed, permitting the increment of the water holding capacity.

The parameter "p" did not significantly change. It means that despite the ultrasound treatment, the fraction of water absorbed in each step of the process was the same (Figure 5.4). This parameter was called as "shape factor" by Verma et al.

(1985) and they stated that this parameter did not change during the drying process at different temperatures. Therefore, it is a characteristic parameter of the grain, related with its structure and composition. As this parameter was not changed, it means that the ultrasound did not change the structure of the corn grains. In fact, it is in accordance with the non-formation of micro channels during the ultrasound-assisted hydration of corn kernels (agreement among the results of hydration processes, mathematical modeling and microstructure).

The parameter k_8 is related to the first step of the process, when probably the capillary flow is predominant. It did not significantly change with the application of ultrasound. The hydration of the kernels in the first step is too fast due to the capillarity that the possible enhancement caused by the ultrasound was insignificant. On the other hand, the parameter k_9, which is related to the second step of the process, where the diffusion is predominant, was significantly increased (30 %). The area for water diffusion is too large in the second step since the water is transferred from the bulk water, the spaces between the germ and endosperm and between the endosperm and pericarp. The ultrasound kept the water supply for the diffusional phenomena since the porosity and spaces inside the kernels kept full of water by the direct effects, explaining the increase of k_9.

In conclusion, it was proved that the ultrasound technology enhances the hydration of corn kernels, accelerating the process and increasing the equilibrium moisture. Even though, it is important to evaluate the impact of this technology on the grain starch properties.

5.3.5 Effect of the ultrasound technology on the starch properties

The starch extracted from the corn kernels hydrated with and without ultrasound was analyzed in order to verify any changes on its properties. Table 5.2 and Figure 4.8 show no significant different among the results of RVA, DSC and X-ray diffraction. In addition, the structure of the starch was not changed as the SEM images show (Figure 5.9). It means that the ultrasound-assisted hydration did not affect the starch properties of the corn in relation to the conventional process.

Table 5.2 – Analysis of the starch extracted from corn kernels conventional hydrated and with ultrasound (mean values ± standard deviation). The letters next to the values represent the mean comparison of Tukey test ($p<0.05$)

Analysis	**Result**	**Starch sample**	
		Conventional hydration	**With Ultrasound**
RVA	Peak 1 (mPa.s)	2618.25 ± 33.54[a]	2629.25 ± 13.12[a]
	Trough 1 (mPa.s)	1619 ± 46.15[a]	1665 ± 39.35[a]
	Breakdown (mPa.s)	999.25 ± 48.42[a]	964.25 ± 40.93[a]
	Final apparent viscosity (mPa.s)	3305.5 ± 41.4[a]	3407.25 ± 21.7[a]
	Setback (mPa.s)	1686.5 ± 34.72[a]	1742.25 ± 39.25[a]
	Peak Time (min)	8.58 ± 0.04[a]	8.63 ± 0.09[a]
	Pasting Temperature (°C)	71.14 ± 0.06[a]	71.5 ± 0.45[a]
DSC	Pasting Temperature (°C)	72.73 ± 0.01[a]	73.46 ± 0.08[a]
	Pasting enthalpy (kJ/kg)	-13.1 ± 0.92[a]	-11.95 ± 0.69[a]
X-ray diffraction	Relative Cristallinity	20.4 ± 0.4[a]	20.2 ± 0.6[a]

In contrast, previous works demonstrated that the ultrasound technology affects the starch granules when they are freely in a suspension and the ultrasound is directly applied, modifying the pasting and thermal properties and damaging its structure (AMINI; RAZAVI; MORTAZAVI, 2015; SUJKA; JAMROZ, 2013; ZHU et al., 2012). However, when the starch is packed into the cells of the endosperm of the corn kernels, it is probable protected from the acoustic cavitation due to its compactness, explaining the results here observed.

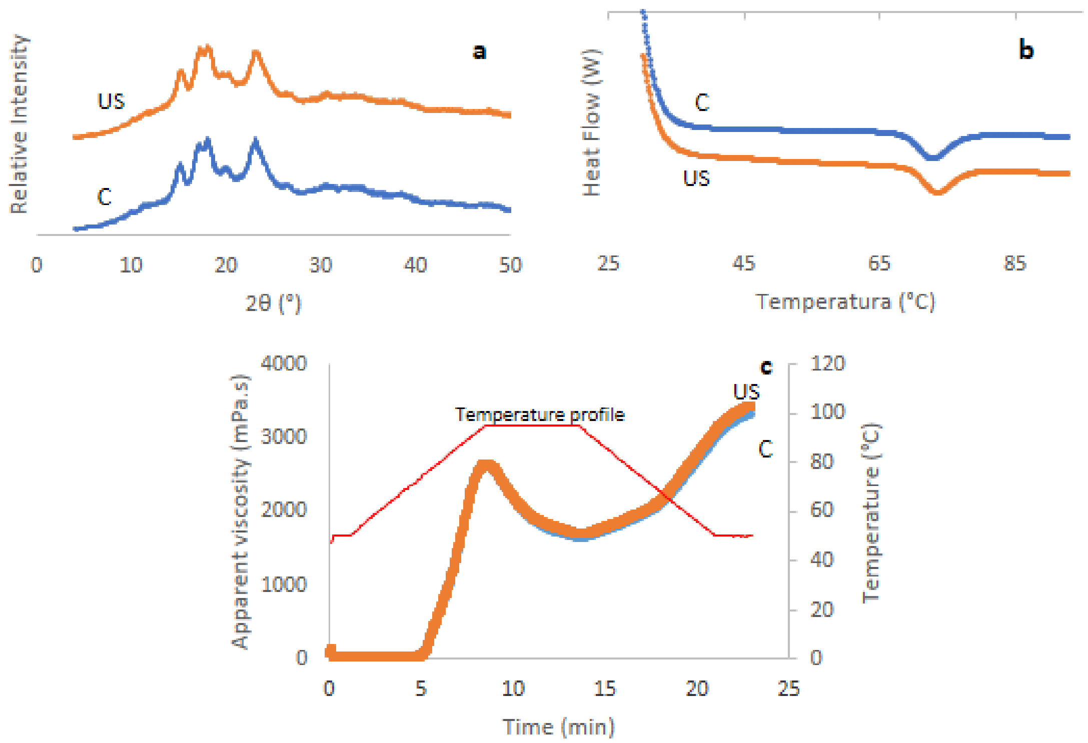

Figure 5.8 – Evaluation of the cornstarch properties extracted from corn kernels conventionally hydrated (C) and with ultrasound (US). a. X-ray diffraction profile, b. DSC profile and c. RVA profile

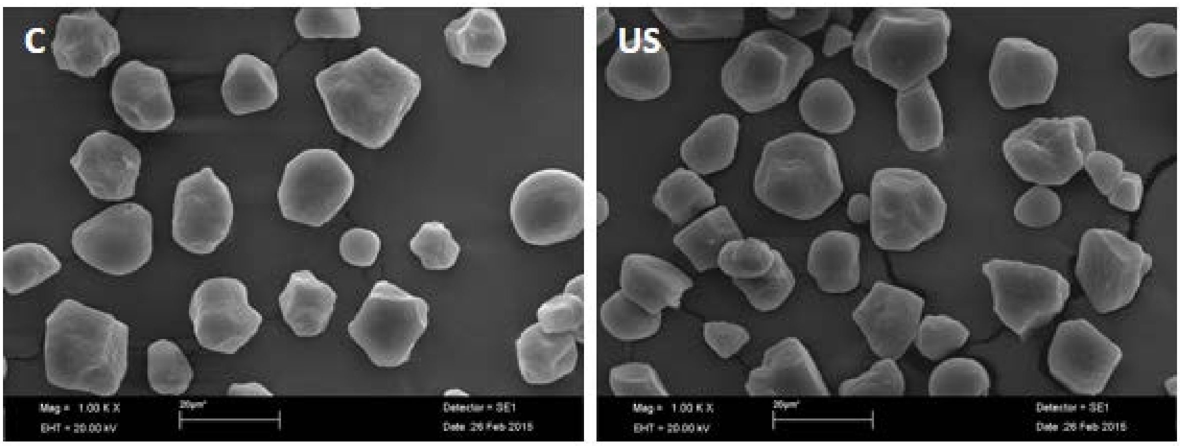

Figure 5.9 – Evaluation of the cornstarch microstructure extracted from corn kernels conventionally hydrated (C) and with ultrasound (US). (SEM, 20 kV; the magnifications are shown in the figure)

Any work has evaluated the effect of the ultrasound technology during the hydration process of grains in its starch properties. In fact, only the pasting properties of navy beans flour that was hydrated with ultrasound was studied (GHAFOOR et al., 2014). In that work, the apparent viscosity was increased by ultrasound. However, the navy beans flour is composed not only by starch, but also by proteins and also others components. In addition, the quantity of starch is ~23 % (HOOVER; RATNAYAKE, 2002) comparing to corn kernels that is ~73 %. Therefore, that apparent viscosity increase could be due to the other components modification, such as proteins, and not by the modification of the starch.

Therefore, it can be concluded that the corn kernels can be hydrated using the ultrasound technology without affecting the quality of the starch. In fact, it is a highly relevant and desirable result in an industrial point of view.

5.4 Conclusions

The ultrasound technology enhances the hydration process of corn kernels, reducing in ~35% the process time. It was demonstrated that the improvement of the process was due to the direct effects caused by the ultrasound and not to the micro channels formation. Moreover, since the corn kernels hydrate by capillarity and diffusion in a two-steps process, it was proposed a suitable model (two terms equation) to explain the hydration process. Finally, the pasting, thermal and structural properties of the obtained starch were compared, demonstrating no significant difference between the hydrated corn kernels (with and without ultrasound). Therefore, the hydration process of corn kernels can be improved using the ultrasound technology without changing their starch quality. It is highlighted that the obtained results show a high relevance both from a scientific and industrial point of views.

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6 GENERAL CONCLUSIONS

The present work evaluated different aspects of the grain hydration process, in order to better understand it and improve it.

The hydration process of three grains was described and modeled: Andean lupin (*Lupinus mutabilis*), Adzuki beans (*Vigna angularis*) and Corn Kernels (*Zea mays*). It was proven that the entrance of water into the grain is not a mere diffusion mechanism since they have a complex structure (morphology), it is also related with capillarity and specific pathways. As a result, there are grains such as Andean lupin and Adzuki beans that have sigmoidal behavior of hydration and others such a corn kernels that has downward concave shape behavior of hydration. Therefore, this has to be taken into account when the process is going to be described, modeled and optimized.

It was established how water is transferred inside the studied grains was established. In the case of Andean lupin and Adzuki beans (sigmoidal behavior), the water enters through the hilar fissure by capillarity and through the seed coat by diffusion. However, the seed coat is less permeable to water in some grains, whose permeability changes during the process. At low water activity, the water enters only by the hilar fissure. When the seed coat is hydrated, it becomes more permeable, letting the water enters and accelerating the hydration process. For those reasons, it was proven that the seed coat is the cause of the sigmoidal behavior in different grains. The cotyledons are hydrated until reach the equilibrium moisture. For the corn kernels (downward concave shape behavior), the water enters simultaneously by the tip cap and by the pericarp. The pericarp of the corn kernel is analogous to the seed coat of the legumes; however, it is more permeable to water. Furthermore, the tip cap is very porous causing the water to enter very fast in the first part of the process. The endosperm is hydrated lately, and due to its compactness, it takes long times.

The mathematical modeling of this process may be tricky. Therefore, the better model that fit with the behavior of hydration of the grain must be evaluated not only by the statistical adjustment, but also by describing the process adequately. For example, it is very important that the mathematical models have explainable parameters in a physical way. For sigmoidal behavior grains, Kaptso et al. ;odel was very versatile. It has explainable parameters, and it was demonstrated that it fits very well for Andean lupin and Adzuky beans. For downward concave behavior grains, the most used mathematical model is the Peleg Model. However, it was proved that for corn kernels it did not appropriately fit. Thus, a model was proposed and explained for this grain.

The hydration is a discontinuous process that takes long times, whose enhancement is desirable. For that reason, traditional technologies were firstly evaluated to enhance this process. The effect of the soaking water temperature and initial moisture content of the grain were evaluated in relation to the hydration kinetics, correlated the results with the morphology and mathematical models.

The effect of the temperature was evaluated for the Andean lupin, while the effect of the initial moisture content was evaluated for Adzuki beans. The higher the temperature is, the shorter the hydration time is, increasing the equilibrium moisture content and the hydration rate, and reducing the lag phase. The initial moisture content of the grain is one of the responsible of the hydration behavior. As the initial moisture content is reduced, larger is the lag phase of the sigmoidal curve. However, when the initial moisture content pass from a specific value (water activity related with ~20 % d.b. for Adzuki beans) the behavior of hydration change from sigmoidal shape to downward concave shape.

Furthermore, a non-conventional technology was studied in order to improve the hydration process. In this case, the ultrasound was demonstrated as promising technology. For that, the mechanisms (direct and indirect effects) of how ultrasound enhances the mass transfer in food with different water activities were studied. It was demonstrated that in dry food, the mass transfer is only improved by the direct effects (sponge effect and inertial flow) and in moist food the mass transfer is improved by both direct effects and indirect effects (micro channels formation by the acoustic cavitation) since the high water vapor pressure permits the acoustic cavitation to takes place. This was a very interesting result, allowing the application of this technology only when it can be maximized its effect during the hydration process.

In the corn kernel hydration process, it was demonstrated that ultrasound technology improved the process reducing its time almost 35 %, without changing rheological, thermal, and structural properties of its starch. Moreover, considering the previous work, the mechanisms of enhancement of the mass transfer in this grain were determined. The ultrasound technology improves the hydration process on corn kernels only by direct effects.

As a conclusion, it is highlighted that these results are very relevant for the industry, since the hydration process may be improved without modifying the properties of its main product (starch), as well as for the academic, since it may help to explain better the hydration process and to explain how ultrasound acts when it improves the mass transfer process. For instance, by knowing which technology to use and in which part of the process it has to be applied, the process can be more efficient, mainly reducing the process time.

7 SUGGESTIONS FOR FUTURE RESEARCH

In future research works, the effect of the ultrasound technology on the behavior of the hydration process of different grains can be studied, especially for sigmoidal behavior hydration. It can be studied if the initial moisture content that changes the behavior from sigmoidal shape to downward concave shape is affected with ultrasound.

In addition, it can be studied the effect of ultrasound in the hydration process of other grains (cereals, legumes or other species) since the morphology (and, consequently, the water flow pathway, mechanisms of mass transfer improvement, etc.) is different in each grain.

Further, the effect of the ultrasound technology on other components of the grains such as proteins, lipids and vitamins can be studied. Moreover, it can be study if the following process is affected when the ultrasound is used during the hydration such as germination, extraction and fermentation.

Finally, the effect of other novel technology also can be studied for improving the grain hydration process: high hydrostatic pressures, electric pulses, irradiation, etc. (isolated or in combination).

APPENDIX

Appendix A – Abstracts in Portuguese and Spanish

Chapter 2. CORRELATION BETWEEN MORPHOLOGY, HYDRATION KINETICS AND MATHEMATICAL MODELS ON ANDEAN LUPIN (*Lupinus mutabilis* Sweet) GRAINS

Português

O presente trabalho descreveu a cinética de hidratação de grãos de tremoço andino (*Lupinus mutabilis* Sweet), correlacionando sua morfologia com modelos matemáticos para explicar o processo. Foram realizadas análise microestruturais utilizando microscopia eletrônica de varredura e foi determinada a cinética de hidratação entre 23°C e 60°C. A cinética de hidratação apresentou um comportamento sigmoidal, o qual foi ajustado em dois modelos sigmoidais. Ainda, este comportamento foi explicado com a morfologia do grão, demostrando que a casca é a causa deste comportamento, relacionado como a lenta taxa inicial de hidratação. Foi demostrado que a água entra no grão por difusão através da casca e por capilaridade através do hilo. Além disso, o incremento da temperatura do processo resultou em um aumento da taxa de hidratação, diminuição do tempo de hidratação e aumento do conteúdo final de umidade, melhorando o processo. Cada parâmetro dos modelos (umidade de equilíbrio, taxa de absorção de agua e tempo de fase lag) foi modelado como função da temperatura. Finalmente, dois modelos gerais foram obtidos com um bom ajuste, os quais podem ser usados para prever o conteúdo de umidade dos grãos como função do tempo e temperatura.

Palavras-chave: Tremoço andino; Hidratação; Modelamento; Morfologia; Reidratação

Español

El presente trabajo describe la cinética de hidratación de los granos de tarwi (*Lupinus mutabilis* Sweet), correlacionando su morfología con modelos matemáticos para explicar este proceso. Para lo cual, se analizó la microestructura de los granos usando Microscopía Electrónica de Barrido, así como el modelamiento matemático de la cinética de hidratación entre 23 °C y 60 °C. La cinética de hidratación del tarwi tuvo un comportamiento sigmoideo, el cual fue modelado usando dos modelos. Además, este comportamiento fue explicado con la morfología del grano, demostrando que la testa fue la causante de dicho comportamiento relacionado con la lenta absorción inicial de agua. También se demostró que el agua entra en el grano de tarwi por difusión a través de la testa y por capilaridad a través de la fisura hilar. Por otro lado, el incremento de la temperatura del agua de remojo aumentó la tasa de absorción de agua, disminuyó el tiempo de hidratación y aumentó la máxima humedad absorbida, lo cual mejoró el proceso. Cada parámetro de los modelos (humedad de equilibrio, tasa de absorción de agua y tiempo de fase lag) fueron modelados en función del tiempo. Finalmente, dos modelos generales fueron obtenidos los cuales fueron usados para predecir la humedad de los granos en función del tiempo y la temperatura.

Palabras clave: Tarwi; Hidratación; Modelamiento; Morfología; Rehidratación

Chapter 3. FROM THE SIGMOIDAL TO THE DOWNWARD CONCAVE SHAPE BEHAVIOR DURING THE HYDRATION OF GRAINS: EFFECT OF THE INITIAL MOISTURE CONTENT ON ADZUKI BEANS (*Vigna angularis*)

Português

Este trabalho estudou a mudança de comportamento de hidratação do feijão Adzuki (*Vigna angularis*) em função do seu conteúdo inicial de umidade. Estudando a cinética de hidratação em diferentes conteúdos iniciais de umidade, foi demostrado que o comportamento de hidratação dos grãos muda de forma sigmoidal para côncava para baixo (DCS) quando o conteúdo inicial de umidade é acima de ~20 % b.s. Esta mudança acontece quando o conteúdo de umidade passa da zona II para a zona III da isoterma de sorção dos grãos. Este comportamento foi atribuído à transição de estado vítreo para estado gomoso, especialmente dos componentes da casca. A casca é impermeável quando o conteúdo de umidade do grão é baixa, quando a água entra somente pelo hilo. No entanto, quando a casca tem o conteudo de umidade maior a ~20 % b.s., a água entra tanto pelo hilo como pela casca. O comportamento de hidratação do grão foi modelado usando um modelo matemático sigmoidal, onde seus parâmetros foram avaliados em função do conteúdo inicial de umidade. O parâmetro da taxa de absorção de agua demostrou um incremento sigmoidal; o tempo para alcançar o ponto de inflexão da curva, relacionado com o tempo lag, mostrou uma redução exponencial; a umidade de equilíbrio não foi afetada. Finalmente, foi obtido um modelo geral que pode ser usado para prever o conteúdo de umidade em função do conteúdo inicial de umidade do grão e o tempo do processo.

Palavras-chave: Hidratação; Modelamento; Feijão adzuki; Reidratação

Español

El presente trabajo estudió el cambio de comportamiento de hidratación del frejol Adzuki (*Vigna angularis*) en función de su contenido de humedad inicial. Estudiando la cinética de hidratación a diferentes contenidos de humedad inicial, fue demostrado que el comportamiento de hidratación de dichos granos cambia de forma sigmoidea a forma cóncava para abajo (DCS) cuando el contenido de humedad inicial es mayor a ~20 % d.b. Este cambio sucede cuando el contenido de humedad pasa de la zona II a la zona III de la isoterma de absorción del grano, especialmente de los componentes de la testa. La testa es impermeable cuando el contenido de humedad del grano es bajo, por lo que el agua sólo entra por el hilo. Sin embargo, cuando la testa está por debajo de ~20 % d.b. de contenido de humedad, el agua entra no solamente por el hilo, sino también por la testa. El comportamiento de hidratación del grano fue modelado usando un modelo matemático sigmoideo, en que sus parámetros fueron evaluados en función del contenido de humedad inicial. Con el aumento del contenido de humedad inicial, el parámetro de la tasa de absorción de agua se redujo sigmoideamente; el tiempo para alcanzar el punto de inflexión de la curva, relacionado con la fase lag, mostro una caída exponencial; la humedad de equilibrio no fue afectada. Finalmente, fue obtenido un modelo general, el cual fue capaz de predecir el contenido de humedad de los granos en función del tiempo y el contenido de humedad inicial.

Palabras clave: Hidratación; Modelamiento; Frejol adzuki; Rehidratación

Chapter 4. MECHANISMS FOR IMPROVING MASS TRANSFER IN FOOD WITH ULTRASOUND TECHNOLOGY: DESCRIBING THE PHENOMENA IN TWO MODEL CASES

Português

O objetivo do presente trabalho foi demostrar como os mecanismos do ultrassom (efeitos diretos e efeitos indiretos) melhoram o fenômeno de transferência de massa no processado de alimentos, e em que parte do processo ele são mais efetivos. Diferentes tratamentos permitiram avaliar e discriminar os efeitos diretos (fluxo inercial e efeito esponja) e indiretos (formação de micro canais), alternando pré tratamentos e tratamentos e usando um banho de ultrassom (40 kHz de frequência e 28 W/L de potência volumétrica) e um banho tradicional com dois tipos de alimento: grãos de sorgo e cilindros de melão. Foi demostrado que ambos efeitos da tecnologia de ultrassom são mais efetivos em alimentos com alta atividade de água, formando-se somente micro canais neste tipo de alimento. Além disso, a formação de micro canais pôde ser observada usando cilindros de gel de ágar, verificando a formação aleatória pela cavitação acústica. Demonstrou-se que os efeitos diretos são mais importantes na melhora da transferência de massa tanto em alimento úmidos como em alimentos secos, tanto pelos micro canais formados quanto pela porosidade do alimentos. Em conclusão, a melhora da transferência de massa devido aos efeitos diretos e indiretos foi primeiramente discriminada e descrevida. Foi provado que ambos mecanismos são importantes na transferência de massa em alimentos úmidos, enquanto somente os efeitos diretos são importante para alimentos secos. Com base nos resultados, provou-se que o uso da tecnologia do ultrassom pode melhorar os processos de alimentos

Palavras-chave: Ultrassom; Transferência de massa; Micro canais; Efeito esponja; Fluxo inercial

Español

El objetivo de este trabajo fue demostrar como los mecanismos del ultrasonido (efectos directos e indirectos) mejoran el fenómeno de transferencia de materia en el procesado de alimentos, y en que parte del proceso ellos son más efectivos. Diferentes tratamientos permitieron evaluar y discriminar tanto los efectos directos (flujo inercial y efecto esponja) e indirectos (formación de micro canales). Se alternaron pre tratamientos y tratamientos usando un baño de ultrasonido (40 kHz de frecuencia y 28 W/L de potencia volumétrica) y un baño convencional con dos tipos de alimentos: granos de sorgo y cilindros de melón amarillo. Se demostró que ambos efectos del ultrasonido son más efectivos en alimentos con alta actividad de agua, formándose sólo micro canales en alimentos húmedos. Además, la formación de micro canales se pudo también observar en cilindros de gel de agar, verificando la su formación aleatoria debido a la cavitación acústica. Los efectos directos fueron importantes en la mejora de la transferencia de materia no sólo en alimentos húmedos, sino también en alimentos secos, siendo esto mejorado por los micro canales pre formados y la porosidad del alimento. En conclusión, la mejora de la transferencia de materia debido a los efectos directos e indirectos fue por primera vez discriminada y descrita. Se demostró que ambos mecanismos son importantes para la transferencia de materia en alimentos húmedos, mientras que sólo los efectos directos son importantes para alimentos secos. Basados en estos resultados, puede mejorarse el procesamiento de alimentos usando la tecnología de ultrasonido.

Palabras clave: Ultrasonido; Transferencia de materia; Micro canales; Efecto esponja; Flujo inercial

Chapter 5. ULTRASOUND TECHNOLOGY ENHANCES THE HYDRATION OF CORN KERNELS WITHOUT AFFECTING THE STARCH PROPERTIES

Português

No presente trabalho estudou-se o efeito da tecnologia de ultrassom no processo de hidratação de grãos de milho, avaliando a absorção de água pelo grão e as propriedades do amido obtido. Para tal, utilizou-se um banho de ultrassom de 25 kHz de frequência e 41 W/L de potência volumétrica. Diferentes tratamentos foram realizados para se determinar os mecanismos de melhoria do processo de hidratação (efeitos diretos o indiretos), estudando a cinética de hidratação e a microestrutura dos grãos. Finalmente, as propriedades reológicas, térmicas e estruturais do amido do milho hidratado com e sem ultrassom foram avaliadas. Devido ao comportamento específico que os grãos de milho apresentam, propôs-se um modelo matemático de dois termos para explicar o processo, o qual teve duas etapas relacionadas com os diferentes mecanismos de entrada de agua no grão. O ultrassom melhorou significativamente o processo de hidratação, aumentando a taxa de absorção de água e diminuindo o tempo de processo em ~35%. Diferentemente de outros grãos, foi demostrado que a melhora do processo foi somente devido aos efeitos diretos (fluxo inercial e efeito esponja) e não devido aos efeitos indiretos (formação de micro canais). Finalmente, provou-se que os grãos de milho podem se hidratar mais rapidamente usando a tecnologia de ultrassom sem a modificação das propriedades do seu amido, sendo tal resultando bastante desejável para a indústria de amido.

Palavras-chave: Ultrassom; Hidratação; Modelagem; Grãos de milho; Amido

Español

En el presente trabajo fue estudiado el efecto de la tecnología del ultrasonido en el proceso de hidratación de granos de maíz, evaluando tanto la como el agua ingresa al grano y las propiedades de su almidón. Para lo cual se empleó un baño de 25 kHz de frecuencia y 41 W/L de potencia volumétrica. Además, diferentes tratamientos fueron realizados para determinar cuáles fueron los mecanismos de mejora (efectos directos o indirectos) causado por el ultrasonido, estudiando también la cinética de hidratación y la microestructura de los granos. Finalmente, se evaluaron las propiedades reológicas, térmicas y estructurales del almidón de los granos de maíz hidratados con y sin ultrasonido. Debido al comportamiento particular de hidratación que tenían los granos de maíz, un modelo de dos términos fue propuesto para explicar el proceso, el cual tenía dos maneras simultáneas relacionadas a los diferentes mecanismos de transferencia del agua. Finalmente, fue demostrado que la tecnología de ultrasonido no cambió las propiedades del almidón. Como conclusión se probó que los granos de maíz pueden ser hidratados usando ultrasonido sin afectar las propiedades de su almidón, siendo muy deseable para la industria del almidón.

Palabras clave: Ultrasonido; Hidratación; Modelado; Granos de maíz; Almidón

Appendix B - Simple abstract

English

The hydration is a very important step during many food processes, such as grains. It is a discontinuous and time-consuming step; therefore, being limiting for the food industry. In the present work, the hydration process of grains was studied, described and improved using the ultrasound technology. It was established the water entrance pathway in the grains, correlating it with the hydration kinetics, mathematical models and the grain morphology. In addition, it was studied how the temperature of the soaking water and the initial moisture content of the grain affect the hydration process. Finally, it was demonstrated that ultrasound technology significantly enhances the hydration process without affecting the grains component properties, also demonstrating what mechanism of this technology are the cause of this improvement. Therefore, the efficiency of the hydration process was improved.

Keywords: Hydration; Rehydration; Unit operations; Mass transfer; Ultrasound; Novel technologies; Process engineering

Português

O processo de hidratação é uma etapa de grande importância no processamento de alimentos, como grãos. É uma etapa descontínua e demorada, sendo, portanto, limitante para a indústria de alimentos. No presente trabalho, o processo de hidratação de grãos foi estudado, descrito e melhorado usando a tecnologia de ultrassom. Estabeleceu-se a rota como a água entra nos grãos, correlacionando-se a cinética de hidratação com os modelos matemáticos e com a morfologia dos grãos. Além disso, estudou-se o efeito da temperatura da água de remolho e o conteúdo de água inicial do grão no processo de hidratação. Por fim, demonstrou-se que a tecnologia de ultrassom melhora significativamente o processo de hidratação sem afetar as propriedades dos componentes do grão, demonstrando-se os mecanismos que resultam nessa melhora. Portanto, a eficiência do processo de hidratação foi melhorada.

Palavras-chave: Hidratação; Reidratação; Operações unitárias; Transferência de massa; Ultrassom; Novas tecnologias; Engenharia de processos

Español

El proceso de hidratación es una etapa de gran importancia en el procesamiento de alimentos, como por ejemplo en granos. Es una etapa discontinua y demorada, siendo, por lo tanto, limitante para la industria de alimentos. En el presente trabajo, el proceso de hidratación de granos fue estudiado, descrito y mejorado usando la tecnología de ultrasonido. Se estableció la ruta de entrada de agua en los granos, correlacionando la cinética de hidratación con modelos matemáticos y con la morfología de ellos. Además, fue estudiado como afecta la temperatura del agua de remojo y la humedad inicial de grano al proceso. También, se demostró que la tecnología de ultrasonido mejora significativamente el proceso de hidratación sin afectar las propiedades de los componentes del grano, y fue demostrado también, qué mecanismos de esta tecnología fueron la causa de esta mejora. Por lo tanto la eficiencia del proceso de hidratación fue mejorada.

Palabras clave: Hidratación; Rehidratación; Transferencia de materia; Ultrasonido; Nuevas tecnologías; Ingeniería de procesos

Appendix C - First page of the published Chapter 2

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Correlation between morphology, hydration kinetics and mathematical models on Andean lupin (*Lupinus mutabilis* Sweet) grains

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ABSTRACT

This work describes the hydration kinetics of Andean lupin (*Lupinus mutabilis* Sweet) grains, correlating its morphology with mathematical models in order to explain the process. Microstructural analysis of the grains was performed using a scanning electron microscope and the hydration kinetics was determined between 23 °C and 60 °C. The hydration kinetics showed the sigmoidal behavior, which was fitted with two sigmoidal models. Further, this behavior was explained by the grain morphology, demonstrating that the seed coat was the cause of this behavior, related to the slow initial water intake. It was demonstrated that the water entered to the grain by diffusion through the seed coat, and by capillarity through the hilar fissure. Besides, an increase in the process temperature resulted in higher water absorption rate, smaller hydration time and higher final moisture content, enhancing the process. Each model's parameter (equilibrium moisture, water absorption rate and lag phase time) was then modeled as function of the temperature. Finally, two general models were obtained with good agreement, which can be used to predict the moisture of the grain as function of both time and temperature.

1. Introduction

The Andean lupin, also called Chocho or Tarwi (NRC-US, 1989) is a legume from the Andean region, of South America, which is widely used by the local population as food and natural medicine (Jacobsen & Mujica, 2006). It is known by its high nutritional value, with a high content of proteins (44.3 g/100 g) and unsaturated fatty acids (40.4 g/100 g of omega-9, 37.1 g/100 g of omega-6 and 2.9 g/100 g of omega-3, with respect to the total fat content – 16.5 g/100 g) (Jacobsen & Mujica, 2006). It is used mainly as a protein source in human and animal nutrition in various parts of the world, and its consumption has increased in recent years (Güémes-Vera, Peña-Bautista, Jiménez-Martínez, Dávila-Ortiz, & Calderón-Domínguez, 2008). This grain is being considered an internationally promising crop, especially in Peru, where its production is growing since it started to be incentivized (Brigas Céspedes, 2014; Mohme Seminario, 2014).

The hydration process in grains is a prior step to different processes such as cooking, extraction, germination and wet milling, since it prepares the grains for processing. In most cases, this stage is a batch unit operation, with a long duration (between 4 and 18 h on average). Many studies have already been conducted about the hydration of different grains, such as adzuki beans (Oliveira et al., 2013), chickpeas (Gowen, Abu-Ghannam, Frias, & Oliveira, 2007; Ibarz, González, & Barbosa-Cánovas, 2004; Yildirim, Öner, & Bayram, 2011), white lupin (Solomon, 2009), red kidney beans (Abu-Ghannam & McKenna, 1997a, 1997b), sesame seeds (Khazaei & Mohammadi, 2009), and so on. However, most of these works just evaluated the grain hydration using simple kinetics models, neglecting the initial lag phase that some grains have. The few studies that considered sigmoidal hydration kinetics for grains neither ensure the cause of lag phase nor explain the process morphologically giving only suppositions. Further, there is not any work in the literature studying the hydration kinetics of Andean lupin (*Lupinus mutabilis* Sweet), despite that it is an important stage because it increases the water content of the grain and enhances the alkaloids extraction in the subsequent stages (Carvajal-Larenas, Nout, van Boekel, Koziol, & Linnemann, 2013).

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From the sigmoidal to the downward concave shape behavior during the hydration of grains: Effect of the initial moisture content on Adzuki beans (*Vigna angularis*)☆

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ABSTRACT

This work studied the change of the hydration behavior of Adzuki beans (*Vigna angularis*) as a function of their initial moisture content. By studying the hydration kinetics at different initial moisture contents, it was demonstrated that the hydration behavior of this grain changes from the sigmoidal to the downward concave shape (DCS) when the initial moisture content is above ~20% d.b. This change happens when the moisture content passes from zone II to zone III of the grain's adsorption isotherm. This was attributed to the transition from the glassy state to the rubbery state, especially the in seed coat components. The seed coat is impermeable when the moisture content of the grain is low, so the water ingress is only by way of the hilum. However, when the seed coat is above ~20% d.b. the water enters not only via the hilum, but also by way of the seed coat. The hydration behavior of the grain was modeled using a sigmoidal mathematical model, whose parameters were evaluated as a function of the initial moisture content; the water absorption rate parameter demonstrated a sigmoidal increasing behavior. The time to reach the inflexion point of the curve, related to the lag phase, showed an exponential decay. The equilibrium moisture content was not affected. Finally, a general model, which was able to predict the moisture content as a function of the initial moisture content of the grain and the process time, was obtained.

1. Introduction

The grain soaking process is an important step during industrialization since it is one of the first steps in many grain processes. For instance, this process is performed to reduce cooking time, to facilitate starch gelatinization and protein denaturation, and to facilitate the extraction of some components (starch, protein, phenols, tannins, etc.) (Siddiq et al., 2011; Abu-Ghannam, 1998; Deshpande and Bal, 2001). Moreover, this process is used before germination (Singh and Eckhoff, 1996) and fermentation (Egounlety and Aworh, 2003).

The water uptake of the grains can show two forms of behavior, which are differentiated by the mass transfer rate at the beginning of the process (Fig. 1). In the downward concave shape (DCS) behavior, the water influx rate is a maximum at the beginning of the process (at $t \to 0$), falling to zero after enough time has elapsed (at $t \to \infty$) to reach the product equilibrium moisture content (M_{eq}). Among many models, the Peleg Model (Peleg, 1988) is the most widely used equation to describe this behavior. The sigmoidal behavior is described by an initial lag phase, i.e., an initial phase with a low water uptake rate. In this case, the water influx rate firstly increases,

☆ By describing an important process for pulses industralization, the authors pay tribute to the International Year of Pulses (FAO 2016).

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