Quality Assurance and Safety of Crops & Foods, 2015; 7 (4): 459-468

Wageningen Academic Publishers

Gelatinisation kinetics of corn and chickpea starches using DSC, RVA and dynamic rheometry

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Received: 3 December 2013 / Accepted: 12 May 2014

RESEARCH ARTICLE

Abstract

The gelatinisation kinetics (non-isothermal) of corn and chickpea starches at different heating rates were calculated using differential scanning calorimetry (DSC), rapid visco analyser (RVA), and oscillatory dynamic rheometry. The data obtained from the DSC thermogram and the RVA profiles were fitted to Kissinger's and Ozawa's methods. Starch gelatinisation was characterised by two phases, where the first corresponded to the unfolding of amorphous region of the starch granule and the other represented the melting crystalline part. The temperature that separates the unfolding and melting of the granule parts, the breaking temperature, was recorded. Higher activation energy (Ea) was calculated for the DSC data versus the RVA. The Ea values calculated by Kissinger's method indicated that one can use either DSC or RVA to get a comparable Ea for both starches, whereas Ozawa's method showed comparable results for chickpea starch and less comparable for corn starch. The Ea of corn starch as calculated by dynamic rheometry (549 kJ/mol) was comparable.

Keywords: starch, corn, chickpea, kinetics, RVA, DSC

1. Introduction

Starch phase transitions during gelatinisation, which lead gradually to paste formation are considered three stage processes. Water absorption, amylose in the amorphous regions starts leaching out and granules rupture completely and lose birefringence (Ratnayake and Jackson, 2007). Starch gelatinisation can be monitored by differential scanning calorimetry (DSC), rapid visco analyser (RVA), rheometry and others. Chickpea starch contains an average of 29.2% amylose depending on the variety, while corn averages 32% amylose and the rest is amylopectin (Yañez-Farias *et al.*, 1997). Most legumes starches have smooth surface and irregular shape that varied between round and oval, where the length and the width of chickpea starch granule was reported to be 12-31 and 12-20 μm, respectively (Chung *et al.*, 2008). The same authors reported more short glucose chains with degree of polymerisation DP 6-12 and fewer 13-25 or 25-36 DP. The X-ray diffraction profile of chickpea starch was reported to be mostly C-type which is a mix of A and B, while corn starch displayed A-type X-ray diffraction pattern.

Although a number of researchers reported on starch gelatinisation kinetics in excess water (Ahmed and Auras, 2011; Ahmad and Williams, 1999; Ahmed *et al.*, 2008; Israkarn *et al.*, 2007; Slade and Levine, 1991), little has been done on chickpea starch. Frequently, DSC has been used for starch gelatinisation kinetics by reporting gelatinisation enthalpy and peak temperature (Baik *et al.*, 1997; Riva *et al.*, 1994; Spigno and De Faveri, 2004). Using DSC for starch gelatinisation temperature might just give accurate results, according to Jasim (2012), compared with rheometric methods, because starch gelatinisation temperature is mainly dependent on starch water ratio in the absence of stirring and the results might not represent the whole sample because of the uneven water distribution throughout the sample. In addition, DSC considers the final step of gelatinisation to determine gelatinisation temperature because it measures the heat flow at the end

of the granules disruption, whereas rheometric methods take into account changes in the volume of starch-granule fractions as affected by the free space between granules from the beginning to end of gelatinisation.

Chickpea and corn starch gelatinisation kinetics can be determined by DSC according to Ozawa (1970), who demonstrated that non-isothermal DSC data can be used to determine activation energy, with the assumption that peak temperature of starch gelatinisation determined by DSC is also the temperature of the maximum reaction rate. In addition, activation energy and break temperature are also important concepts needed for understanding starch gelatinisation kinetics. Other researcher found close relationship between activation energies estimated using dynamic rheology and optical microscopy. Teyssandier *et al.* (2011) and Okechukwu and Anandha Rao (1996) reported that apparent activation energies were estimated from rheological data (volume fraction phenomenon) and from optical microscopy data and were found to be nearly the same, 110 and 100 kJ/mol, respectively. For instance, increase in granule volume due to hydration of the amorphous region can cause breaking of the secondary bonds that hold the crystalline region together causing drop on the activation energies (Ea). The Ea of starch is greatly affected by the starch-water ratio, where the least needed Ea for starch gelatinisation was reported at 45% water content (Kim and Wang, 1999; Mendes da Silva *et al.*, 1996).

The need for two steps to describe starch gelatinisation process was first quantified and introduced by Suzuki *et al.* (1976) for rice starch, and was confirmed by other researchers (Bakshi and Singh, 1980; Bhavesh and Koushik, 2006; Freitas *et al.*, 2004; Juliano and Pérez, 1986; Ojeda *et al.*, 2000; Pravisani *et al.*, 1985; Yeh and Li, 1996). Therefore, researchers confirmed that starch gelatinisation kinetics is a two-step process (Ojeda *et al.*, 2000; Ozawa, 1970) by introducing the break temperature concept. The break temperature is the temperature that separates the unfolding of the outer layer of the starch granule (amylose) from the melting of the inner crystalline portion (amylopectin). The point where these two temperatures meet is known as the break temperature. Consequently, starch gelatinisation can be expressed as two steps process. The first step describes the increase in the molecular mobility of the amorphous part of the starch granule (rich in amylose) whereas the second step represents the melting of the crystalline region (rich in amylopectin) (Ojeda *et al.*, 2000; Ozawa, 1970).

The objective of this work was to estimate the gelatinisation kinetics of chickpea and corn starch using differential scanning calorimeter (small sample size), rapid visco-analyser (less controlled environment), and dynamic rheology (high sensitivity). The specific objectives were to estimate the apparent Ea of chickpea and corn starches gelatinisation and to observe the effect of the instrumentation type on the final value of Ea. Furthermore, the results may suggest that RVA, a quite simple, economic, and fast technique, is reliable for the determination of Ea of starches.

2. Materials and methods

Materials

Chickpea (*Cicer arietinum* var. *surutato*) starch was isolated from grains obtained from local market. The moisture content of chickpea grain (1 kg) was raised to 25% and left overnight in order to facilitate the removal of the hull by hand prior to milling. Hull-less grain meal was prepared by grinding in a Brabender Laboratory mill SM3 (Brabender® GmbH & Co., Duisburg, Germany). Corn starch was obtained from Tate & Lyle North America, A.E. Staley MFG Co. (Decatur, IL, USA).

Chickpea starch isolation

Hull-free meal was used for preparing slurry of chickpea meal in distilled water (50/50) followed by mixing in heavy duty blender for 5 minutes. The slurry was filtered through 200 mesh sieve (74 microns), where the filtrate was centrifuged at 2,000×*g* for 15 minutes. After centrifugation, the dark colour layer on top was removed and the white pellet at the bottom of the bottle was re-suspended in distilled water and centrifuged as before. This process was repeated 5 times after which a white pure starch fraction was obtained. The isolated starch was mixed with acetone, air-dried, ground in a coffee grinder, placed in air-tight bottles, and stored at 4 °C for later use. The protein and moisture content of the isolated starch were determined using a Foss-NIR Infratec 1241 Grain Analyzer (FOSS, Eden Prairie, MN, USA). The protein content of the isolated starch was 0.07 at 13% moisture content.

Rapid visco analyser measurements

Pasting properties of the corn and chickpea starch, including pasting temperature, were determined using a rapid visco analyser (Newport Scientific, Sydney, Australia). Starch (3 g at 14% moisture basis) was directly weighed into aluminium RVA canisters and distilled water was added to bring the total weight to 28 grams. The obtained slurry was held at 50 °C for 30 seconds, heated to 95 °C at 2, 4, 6, 8, 9, 10, 12, 13, 14 and 16 °C/min, and held at 95 °C for 4 min. It was then cooled to 50 °C using the same rates. The rotating speed of paddle was 960 rpm for first 10 seconds which was reduced to 160 rpm and kept throughout the remainder of the experiment. All measurements were done in triplicate and the Thermocline Windows software (Hägersten, Sweden) was used to process the data.

Differential scanning calorimetry

DSC analysis was conducted to determine the thermal properties of corn and chickpea starch at different heating rates 1, 2, 4, 5, 6, 8, 9, 10, 12, 14, and 16 °C/min using Pyris DSC1 (PerkinElmer, Waltham, MA, USA). Sample (8-10 mg) dry basis was placed in aluminium pans and 16-20 µl distilled water was added, while the reference cell contained suitable amount of distilled water (starch to water ratio was 1:2). After sealing, the sample was equilibrated for 2 h and scanned at the above mentioned heating rates between 25 and 110 °C. Peak temperature was determined using DSC Pyris DSC 1 software (PerkinElmer, Akron, OH, USA).

Rheology measurements

The rheological testing was done only on corn starch, where starch was suspended in de-ionised water at 10% (w/w). The starch dispersion was stored at 4 °C and used for measurements within two days. A strain-controlled TA ARES rheometer (TA instruments, Inc., New Castle, DE, USA) with 50-mm diameter parallel-plates geometry was used to conduct the rheological testing. The sample was placed between the plates with a gap of 1 mm. The temperature was controlled by a water circulation system. To ensure that all the measurements were made within the linear viscoelastic range, a strain-sweep experiment was conducted initially for a completely gelatinised starch. The applied shear strain in the linear range (3%) was adopted for the other viscoelastic property measurements for the remaining starch dispersions whereas fresh samples were used for each experiment. Starch dispersion sample was placed in the centre of the plate at 25 °C and the geometry plates were sealed with mineral oil and covered with a chamber to prevent moisture loss. Samples were equilibrated at least 5 min before conducting the measurements. For the temperature sweep measurements, starch dispersions were heated at different heating rates 0.7, 1, 2, 3, 4, 7, 8, 10, 12, 14, and 16 °C for up to 90 °C at 1 rad/s frequency. Each heating rate experiment was repeated for the fresh sample until the error was within 8%.

Differential scanning calorimetry kinetics

Without a precise knowledge of the reaction mechanism, the activation energy of starch gelatinisation could be determined using Kissinger (1956) or Ozawa (1970) plots.

The Kissinger plot

As also described in Alamri *et al.* (2015), in current kinetic methods the n^{th} reaction order is assumed:

$$\frac{d\alpha}{dt} = k\,(1-\alpha)^n \qquad (1)$$

Where t = time, α = degree of reaction, and n = reaction order.

Considering the outcome of the derivative of the Arrhenius equation and Equation 1, Kissinger hypothetically considered that dα/dt (the reaction rate) is at a maximum at the peak temperature (Tp) of the DSC curve. This temperature is referred to as the starch gelatinisation temperature. Kissinger further assumed that n (1-α)(n-1) is a number close to one, and dT/dt = β (heating rate) a constant, thus:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_p} \qquad (2)$$

The Kissinger equation discloses that for a specific DSC curve with heating rate β, e the maximum reaction rate could be observed at the peak temperature T_p, for a set of DSC curves with varying heating rates. The plot of $\ln(\beta/T_p^2)$ against $1/T_p$ can be applied to get the Kissinger's plot according to Equation 2, where the activation energy Ea is represented by the slope of the line and the pre-exponential factor, A, is the intercept. The linear regression for slope determination was calculated using Sigma Plot (Systat Software, San Jose, CA, USA).

The Ozawa plot

Ozawa (1970) assumed that for the DSC curve the degree of the reaction is constant and independent of the heating rate when the curve reaches its peak. He then derived Equation 3:

$$\ln(\beta) = \text{const} - 1.052\,Ea/R/T_p \qquad (3)$$

Where β = heating rate; Ea = activation energy; R = gas constant; and T_p = peak temperature.

Based on Equation 3, various DSC experiments with different heating rates can be performed and the temperature at the peak of the profile can be determined. The Ozawa plot can be achieved by plotting the log of the heating rate, ln(β), against $1/T_p$, where the activation energy can be determined from the slope of the line. The ASTM E698 approved method for thermal stability is based on Ozawa's equation. For appropriate use of this method, three or more experiments with different heating rates are required.

Dynamic rheology kinetic modelling

The non-isothermal kinetic modelling for a linearly-increasing temperature system was described by Rhim *et al.* (1989). For the n^{th} order reaction, the rate can be expressed as:

$$\frac{-dC}{dt} = kC^n \quad (4)$$

Where C = the concentration; t = time; and k = the rate constant.

For the temperature dependence reaction, the rate constant can be expressed by the Arrhenius relationship:

$$k = k_0 \exp\left(\frac{-Ea}{RT}\right) \quad (5)$$

Where k_0 = the pre-exponential of frequency factor; Ea = the activation energy (J/mol); T = the absolute temperature (K); and R = the universal gas constant (8.314 J/mol K).

Combining Equation 4 and 5 gives:

$$\ln[-(1/C^n)(dC/dt)] = \ln(k_0) - (Ea/R)(1/T) \quad (6)$$

For the rheological kinetics data analysis, C can be replaced with G' even though the elastic modulus (G') relation with concentration is not strictly linear (Jasim, 2012; Yoon *et al.*, 2004). In addition, the relationship between elastic modulus and polymers volume fraction in gels was shown not to affect the outcome of the equations used here as reported by Zrinyi and Horkay (1987). Therefore, Equation 6 can be transformed into:

$$\ln[(1/G'^n)(dG'/dt)] = \ln(k_0) - (Ea/R)(1/T) \quad (7)$$

The negative sign for the concentration in Equation 6 becomes positive in Equation 7 because the value of G' increases during the heating.

Statistics

Analysis of variance was done to show which model fits the data better. The data was analysed as one set in addition to splitting the data into two sets and the Duncan's multiple range test at $P \leq 0.05$ and $P \leq 0.01$ was used to compare means using PASW® Statistics 18 software (SPSS, Quarry Bay, Hong Kong).

3. Results and discussion

DSC is considered one of the methods used for kinetics-parameters calculation in a single stage process. The DSC curve is the fingerprint of the chemical/physical transformation taking place in the reacting system. Conversely, RVA is exclusively used for the determination of starch pasting properties. Therefore, the fundamental assumption in chemical kinetics studies using DSC is that the heat flow, measured in (W/g), is comparative to the baseline and proportional to the reaction rate (Wunderlich, 1990). Consequently, an assumption can be made by considering the pasting temperature obtained during RVA run is the average alteration on this physical property of the starch. Bear in mind that, the pasting temperature given by the RVA is an average temperature between the initial viscosity increase, caused by granule swelling due to hydration, and the maximum viscosity of the system just before granules rupture (break down). The maximum physical change of starch granule, which leads to viscosity increase, signifies leaching out of amylose and disentanglement of the amylopectin within the swollen granule. Therefore, the increase in volume fraction which leads to increase in viscosity is due to higher interaction between starch components (amylose and amylopectin) and water molecules (Keetels and Van Vliet, 1994). Hydration signifies the interaction between starch and water, which is irreversible change of starch granules whereby starch-starch interaction is minimised and substituted by starch-water interaction (Murphy, 2000). Granule swelling and the weakening of starch-starch interaction followed by irreversible granule rupture are the main causes of starch gelatinisation. Normally, DSC experiments are conducted under isothermal (same heating rate) or non-isothermal (different heating rates) conditions. According to appropriate models, kinetics parameters can be calculated from isothermal or dynamic methods based on specific reaction-order and rate constants (Malecki *et al.*, 1998).

The peak viscosity, final viscosity, and set back of corn starch as determined by RVA were 2,438.0±27, 2,677±21 and 1,254.5±71 mPa.s, respectively, whereas chickpea starch exhibited 2,828±92, 4,066.5±194 and 2,471.5±107 mPa.s, respectively. This data showed that the two starches exhibited similar peak viscosity but the final viscosity and the setback for the chickpea were higher. Indicating stronger chickpea starch-gel, this could be due to higher amylose content and water absorption.

The DSC profile of corn starch showed higher peak and onset temperature compared to chickpea, whereas the difference between the peak and onset temperature for both starches was similar. Corn starch showed two peaks for each scan; one was the gelatinisation (at 70 °C) and the other was the melting amylose-lipids complex (at 100.2 °C), whereas chickpea starch did not show lipid-amylose complex melting peak. The DSC scan provided a ΔH (J/g) for corn starch as 12.17±0.13 (0.74±0.21) for lipid complex) and 11.5±0.35 for chickpea.

The DSC and the RVA data shown in Table 1 represent the parameters required for the determination of activation energy according to Kissinger (1956) and Ozawa (1970) for corn and chickpea starches based on Equation 2 and 3. Although calculating Ea was not the main purpose of this work, it was used as common outcome between the methods used, i.e. Ea value was used to determine whether the data generated by DSC, RVA, or rheometry is comparable, thus RVA can be used for Ea determination. The linear regression of the straight line generated from

Table 1. Relationship between peak temperature (T_p) of differential scanning calorimetry and the pasting temperature of the rapid visco analyser at different heating rates of corn and chickpea starches dispersion.

Heating rate (β)	Chickpea			Corn starch		
	Peak T_p(°C)	β/T_p^2 (10^{-5})	$-\ln(\beta/T_p^2\times10^{-5})$	Peak T_p(°C)	β/T_p^2 (10^{-5})	$-\ln(\beta/T_p^2\times10^{-5})$
Differential scanning calorimetry (gelatinisation temperature)						
1	59.07±0.7	0.91	11.61	67.45±0.3	0.86	11.66
2	61.12±1.6	1.79	10.93	68.22±0.9	1.71	10.97
4	61.72±1.8	3.57	10.24	68.56±9.9	2.56	10.57
6	61.95±0.9	5.34	9.84	69.74±7.5	3.40	10.29
8	62.64±2.6	7.09	9.55	70.22±0.5	5.93	9.74
10	63.25±3.8	8.83	9.33	70.31±1.1	6.77	9.59
12	63.80±2.3	10.60	9.16	70.98±0.8	8.44	9.38
14	64.09±3.1	12.30	9.00	71.63±3.2	10.92	9.20
16	64.76±4.3	14.00	8.87	72.07±0.3	11.74	9.05
Rapid visco analyser (pasting temperature)						
2	67.60±2.9	3.44	10.28	72.03±15.1	1.67	10.99
4	68.08±7.3	5.15	9.87	74.98±11.4	3.29	10.32
6	68.53±8.9	6.85	9.59	75.47±9.2	4.94	9.92
8	68.80±10.3	8.55	9.37	76.48±3.5	6.54	9.63
9	69.55±2.3	10.20	9.19	76.68±6.8	7.35	9.52
10	70.23±1.8	11.00	9.11	76.93±7.2	8.16	9.41
12	70.80±2.1	11.80	9.04	77.12±12.3	9.78	9.23
14	70.87±6.8	13.50	8.90	78.58±5.6	11.31	9.09
16	71.08±4.5	15.20	8.79	79.07±6.9	12.89	8.96

the data representing starch gelatinisation from beginning to end showed a low R^2 value indicating bad fit, but when the data was split into two part at specific temperature, the fit was much better which is in agreement with literature reports. Therefore, DSC-corn starch data is reported as >70.2 and <70.2 °C, while DSC-chickpea starch at >62.6 and <62.6 °C. The Ea can be calculated from the Arrhenius relationship by taking the slope of the strait line while the pre-exponential factor will be represented by the intercept of Kissinger plot. Kissinger model was applied to the data collected from DSC or RVA for both starches. When Kissinger model was applied, a plot of $-\ln(\beta/T_p^2\times10^{-5})$ (independent variable) was plotted against $T_p^{-1}(k^{-1})$ (dependent variable) (Table 1). The high coefficient of determination (R^2) indicates that Kissinger plot was suitable for fitting this data. Figure 1, and Table 2, includes the Ea calculated using Kissinger model for both, DSC and RVA. The breaking temperature and the Ea are shown in Table 2. The breaking temperature, as determined by ANOVA, (the temperature that separates the amorphous from crystalline region of the granule) of the RVA data was higher than the DSC for both starches (Table 1 and 2). Corn starch revealed higher Ea determined by either DSC or RVA (Table 2). The Ea above the breaking point (temperature) for both starches and both instruments was higher than below the breaking point which was expected because it represents the Ea for melting the crystalline region of the starch granule. Considering the fact that, DSC testing was done in a hermetically sealed pan versus unsealed RVA canister, i.e. controlled environment plus small sample size of DSC (milligrams) versus stirring and larger sample size (grams) for the RVA. Obviously, the controlled environment is advantage of the DSC since the sample temperature increases in a more uniform way, whereas the larger sample size and agitation in the RVA is a plus because higher sample size reduces the chances for sampling error. In other words, smaller sample size used for the DSC increases the chances for higher error, but that can be minimised by increasing the number of replications. Although RVA sample size was larger, the issue of the unsealed RVA canister can be addressed the same way by executing more runs and maintaining accurate heating rate.

The commonality between the DSC and RVA is that, both samples showed change at specific temperature which is peak temperature for DSC and pasting temperature for RVA, as a function of heating rate. This characteristic allows both instruments to be used for kinetics parameters determination. The higher heating rates of both starches using both instruments resulted in higher peak or pasting temperatures (Table 1). The two instruments were

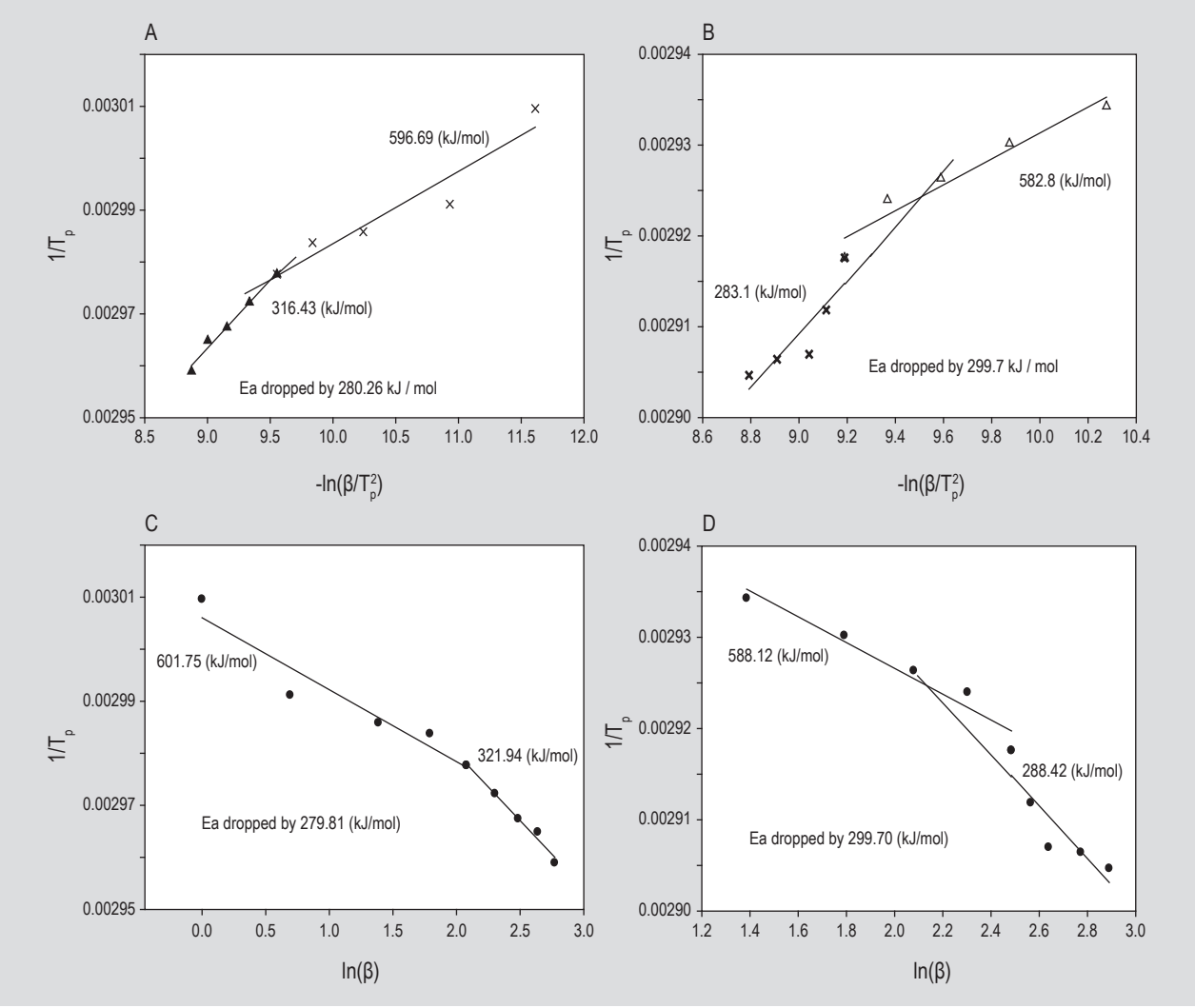

Figure 1. Relationship between heating rates and differential scanning calorimetry (DSC)-peak temperature or rapid visco analyser (RVA)-pasting temperature of chickpea starch gelatinisation according to Kissinger (1956) and Ozawa (1970). (A) DSC-activation energy according to Kissinger. (B) RVA-activation energy according to Kissinger. (C) DSC-activation energy according to Ozawa. (D) RVA-activation energy according to Ozawa. Ea = activation energy.

consistent in showing the differences between the two starches in terms of viscosity parameters and thermal parameters such as peak viscosity and ΔH. Therefore, the higher breaking temperature of RVA can be attributed to the above mentioned difference between the instruments. Higher breaking temperature for corn starch compared to chickpea starch could be attributed to the amylose content granule type, or granule compactness. So that to characterise the difference between the Ea of the amorphous and the crystalline regions of the starch granule, the Ea of the amorphous region was subtracted from the Ea of the crystalline and it was identified as the drop in Ea as shown in Figure 1. In general, we can say that the lower drop in Ea at the breaking point between amorphous and crystalline regions could point to other factors such as hydration rate and is not temperature dependent (Kim and Wang, 1999; Mendes *et al.*, 1996).

The drop in DSC-Ea of Kissinger plot at the breaking temperature for corn starch and chickpea starch was 53.1 and 47.1%, respectively, while the drop of RVA-Ea was 46.1 and 51.4%, respectively (Table 2). The range of Ea drop at the breaking temperature for DSC was 46.1 to 53.1% and for RVA it was 47.1 to 51.4% for corn and chickpea starch, respectively. Due to the closer difference between the drops in Ea (kJ/mol) of the chickpea starch as measured by DSC and RVA, one can use Ozawa plot to determine the Ea of chickpea starch by either DSC or RVA (Figure 1), whereas Kissinger plot gave results with closer differences for chickpea starch and not for corn starch. The calculation of the drop in Ea illustrates the capacity of the instrument to consistently identify the point that separates the amorphous part of the starch granule from the crystalline region.

Table 2. Activation energy (Ea) values for thermal gelatinisation of corn and chickpea starches obtained by fitting first-order rate constant at various heating rates to the Arrhenius equation according to Kissinger (1956) and Ozawa (1970).

	Differential scanning calorimetry (°C)	Activation energy obtained from the slope of the plots (kJ/mol)	Coefficient of determination	Rapid visco analyser (°C)	Activation energy obtained from the slope of the plots (kJ/mol)	Coefficient of determination
Corn starch						
Kissinger 1956[a]	>70.2	647.90	0.94	>76.7	434.61	0.94
	<70.2	304.60	0.99	<76.7	231.42	0.89
Ozawa 1970[b]	>70.2	611.19	0.92	>76.7	333.25	0.97
	<70.2	309.37	0.99	<76.7	236.61	0.90
Chickpea starch						
Kissinger 1956	>62.6	596.69	0.92	>69.6	582.80	0.98
	<62.6	316.43	0.98	<69.6	283.11	0.79
Ozawa 1970	>62.6	601.75	0.91	>69.6	588.12	0.94
	<62.6	321.94	0.98	<69.6	288.42	0.80

[a] Kissinger 1956 = plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ (where β = heating rate; T_p = peak temperature in Kelvin).
[b] Ozawa 1970 = plot of $\ln(\beta)$ versus $1/T_p$.

Similarly, the data was fitted to Ozawa plot, where the ln of the heating rate (ln(β)) was used as independent variable plotted against the reciprocal of the DSC-peak temperature or the RVA-pasting temperature ($1/T_p$). The results of the Ozawa plot showed that the breaking temperature was similar to those of Kissinger (>70.2 and <70.2 °C, DSC) and (>76.7 and <76.7 °C, RVA) for corn starch (Table 2). The Ea calculated using Ozawa model was higher for DSC data versus RVA for both starches, but the DSC data for both starches exhibited similar Ea values (611.19 and 601.75 kJ/mol), whereas RVA data for both starches showed almost twice the Ea of the chickpea starch compared to corn starch, indicating higher heat dependency. That was not observed with Kissinger plot (Table 2).

The range of Ozawa Ea drop of corn starch was 29.1% for DSC and 49.4% for RVA, but chickpea starch exhibited 46.7% and 51.1%. Corn starch exhibited larger difference between DSC and RVA (Table 2). Looking at the difference in range between Kissinger and Ozawa, one can propose the use of Kissinger plot due to the consistency in the range of percent-difference between DSC and RVA for both starches which was much closer than those calculated using Ozawa plot. The reason for the larger range between DSC and RVA for corn starch could be attributed to the amylose content of the two starches, since amylose is located in the amorphous region of the granule; it controls water absorption and thus the melting of the crystalline region. That can be an important factor since stirring that takes place in the RVA. So, lower amylose content can cause the gelatinisation of the starch to be less temperature dependent (low Ea). The activation energies calculated using Ozawa's or Kissinger's methods evidently indicate that above the breaking temperature a change in the starch gelatinisation mechanism takes place.

The rheological properties and gelatinisation kinetics of corn starch were performed at eleven heating rates 0.7, 1, 2, 3, 4, 7, 8, 10, 12, 14, and 16 °C/min. Below 50 °C, the starch dispersion exhibited nearly predominantly viscous properties. Between 60 and 80 °C, the elasticity (G') of the sample rapidly increased until a maximum value was reached (Figure 2). The elastic modulus (G') was decreased slightly with continuous heating. The low elastic modulus (G') at the beginning of heating was due to absolute starch granule integrity with no sign for swelling or rupture. However, the quick increase in G' between 60-80 °C is indicative of water absorption by starch granules, swelling, leaching of amylose and granule disintegration. These events mark the ending of heating and were followed by cooling which causes the conversion of starch to three-dimensional gels due to hydrogen bonding between amylose molecules forming a coherent network (Ahmed and Auras, 2011; Hsu and Huang, 2000; Zhang *et al.*, 2013). At the maximum G' value, G' was designated as G'_{max} and the temperature as gelatinisation T_p. The storage modulus (G') has decreased by further heating beyond T_p, which suggests that the gel structure (network) was disrupted. The starch gel structure disruption might be due to the loss of entanglement of the amylopectin in the swollen particles and weaker interaction between particles. Table 3 displays the gelatinisation T_p for different heating rates, where higher heating rate 0.7 °C/min to 4 °C/min caused higher T_p between 72.9 °C and 85.4 °C, respectively. At heating rates greater than 4 °C/min, the gelatinisation T_p remained around 85 °C due to the limited accuracy of the instrument around rapid heating rate used.

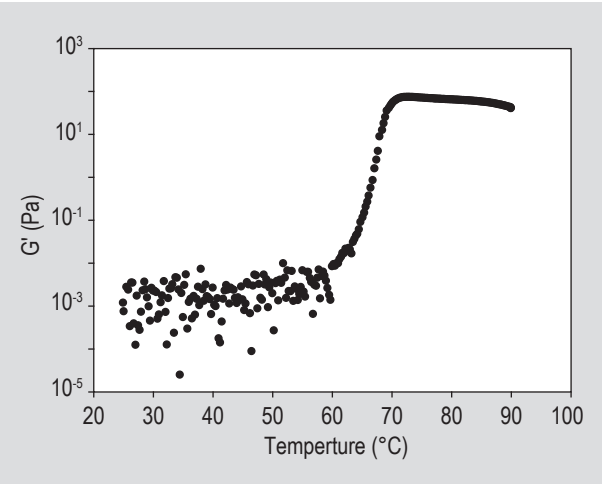

Figure 2. Linear rheological properties of corn starch gelatinisation process performed at 1.0 °C/min heating rate. The elastic (storage) modulus (G') vs. temperature over the temperature sweep measured at frequency of 1 rad/s.

Corn starch reaction order under different heating rate was very interesting. At heating rate of 0.7 °C/min, the data fits well with both first- and second-order reaction kinetics models, but the first-order fitting (R^2=0.92) was better than the second-order one (R^2=0.87) (Figure 3). Figure 4 displays corn starch gelatinisation at 1 °C/min heating rate where the rheological data was found to fit the second-order kinetic model (R^2=0.97) better than the first-order kinetics model (R^2=0.55). Therefore, one can say that, at 0.7 °C/min heating rate, the reaction favours the first-order kinetics model, where at 1 °C/min the second-order model. It is imperative to mention that in the presence of solutes (salts or sugars) the kinetics of starch gelatinisation is mostly dependent on the structure formation induced by starch-solute interaction. For instance, the presence of sugars or salts have direct effect on the starch gelatinisation temperature because these compounds can interact with the water which will have a direct effect on starch gelatinisation temperature thus the gelatinisation kinetics. It appears that, higher heating rate enhances starch-solute interaction so that the gel is formed quicker. The slope of Equation 7 was used to estimate the activation energy. It is generally accepted by researchers that the activation energy is an important parameter needed to investigate the mechanism of a reaction. The calculated activation energy values for corn starch at different heating rates are shown in Table 3. It should be noted that lower activation energy is needed at higher heating rate. At heating rate of 1 °C/min, the estimated Ea was 1,328.4 kJ/mol. However, the calculated Ea decreased to 153 kJ/mol at heating rate of 16 °C/min (Table 3). A wide range of starch activation energy values were reported in the literature (Ahmed *et al.*, 2008).

Table 3. Corn starch gelatinisation reaction activation energy calculated from model fitting $\ln[(1/G'^n)(dG'/dt)]=\ln(k_0)-(Ea/R)(1/T)$.

Heating rate (°C/min)	0.7	1	2	3	4	7	8	10	12	14	16
Activation energy (kJ/mol)	1496.9	1328.4	792.1	641.5	449.1	295.7	234.5	199.5	182.5	177.8	153.0
Coefficient of determination	0.99	0.98	0.80	0.83	0.95	0.89	0.90	0.81	0.98	0.91	0.99

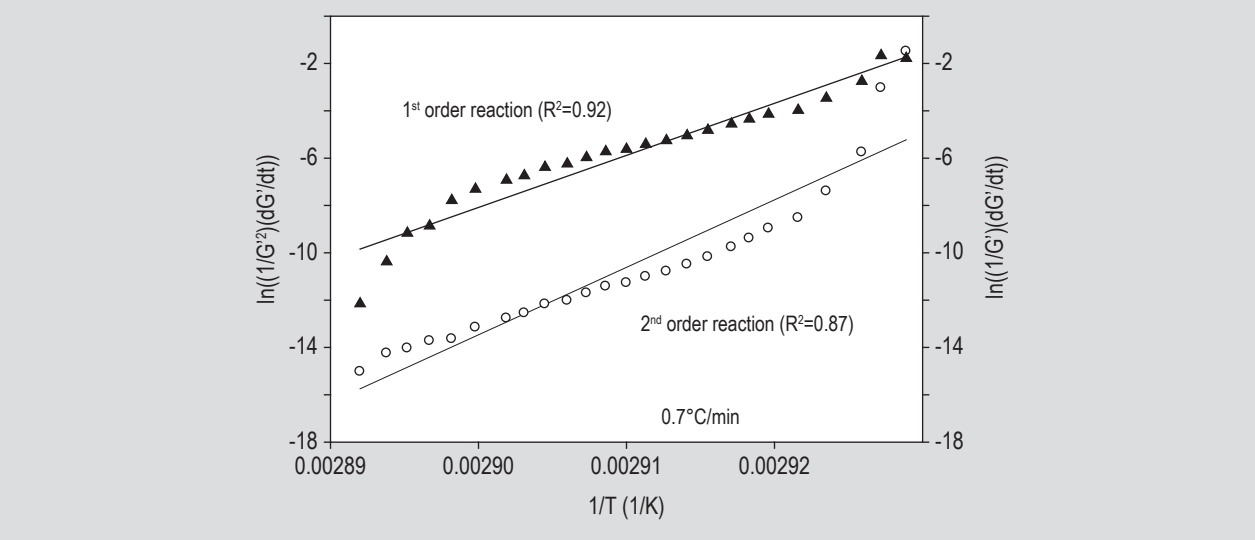

Figure 3. The first- and second-order reaction kinetics fitting of non-isothermal heating of corn starch at 0.7 °C/min heating rate.

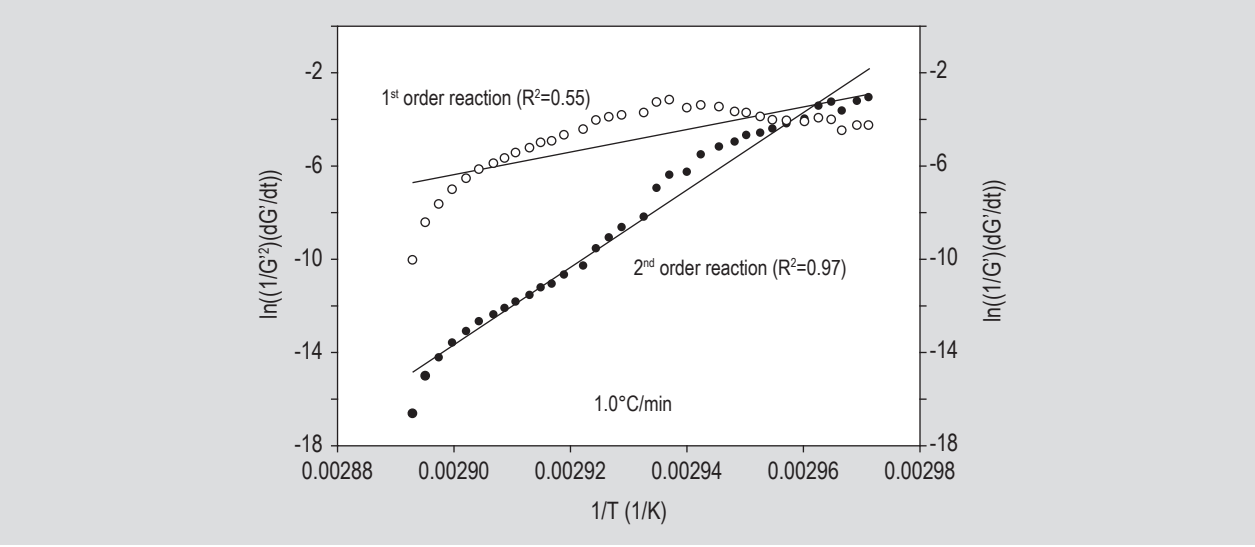

Figure 4. The second- and first-order reaction kinetics fitting of non-isothermal heating of corn starch at heating rate of 1 °C/min.

4. Conclusions

This conclusion concurred with the hypothesis assumed by previous researchers that the DSC peak temperature can be used for estimating the Ea of starch gelatinisation. This study proposed the use of RVA-pasting temperature in lieu of DSC-peak temperature. The results showed that RVA-pasting temperature can be used for Ea calculation since the results were comparable to DSC especially by using Kissinger plot. The break temperature of starch gelatinisation was 70.2 and 76 °C for corn starch and 62.6-69.6 °C for chickpea starch as measured by DSC and RVA, respectively. The rheological data showed that starch gelatinisation kinetic follows first-order reaction when tested at 0.7 °C/min and second-order when measured at 1.0 °C/min. The Ea obtained by rheological model exhibited an average of 549 kJ/mol. The outcome of this study provided a better understanding of chickpea and corn starch gelatinisation kinetics which could lead to improvements and expansion of application of these products. The information obtained here could be used to determine the degree of gelatinisation of starches by comparing the Ea of fully gelatinised starch with unknown sample of the same type of starch. Most importantly, the outcome of this work allows the use of higher sample size and lower cost instrument (RVA) versus smaller sample size and more expensive instrument (DSC). In addition, RVA can provide pasting properties besides gelatinisation kinetics in one run.

Acknowledgements

This project was supported by King Saud University, Deanship of Scientific Research, College of Food & Agricultural Sciences, Research Center (project no. RGP-VPP-114i).

References

Ahmed, F.B. and Williams, P.A., 1999. Effect of sugars on the thermal and rheological properties of sago starch. Biopolymers 50: 401-412.

Ahmed, J. and Auras, R., 2011. Effect of hydrolysis on rheological properties of lentil starch slurry. LWT-Food Science and Technology 44: 976-983.

Ahmed, J., Ramaswamy, H.S., Ayad, A. and Alli, I., 2008. Thermal and dynamic rheology of insoluble starch from Basmati rice. Food Hydrocolloids 22: 278-287.

Alamri, M.S., Hussain, S., Mohamed, A., Al-Ruquie, I.M. and Qasem, A.A.A., 2015. Effect of urea and sodium chloride on the pasting properties and gelatinisation kinetics of corn starch. Quality Assurance and Safety of Crops & Foods 7: 449-457.

Baik, M.Y., Kim, K.J., Cheon, K.C., Ha, Y.C. and Kim, W.S., 1997. Recrystallization kinetics and glass transition of rice starch gel system. Journal of Agricultural and Food Chemistry 45: 4242-4248.

Bakshi, A.S. and Singh, R.P., 1980. Kinetics of water diffusion and starch gelatinization during rice parboiling. Journal of Food Science 45: 1387-1392.

Bhavesh, K.P. and Koushik, S., 2006. Effect of heating rate on starch granule morphology and size. Carbohydrate Polymers. 65: 381-385.

Chung, H.J., Liu, Q., Donner, E., Hoover, R., Warkentin, T.D. and Vandenberg, B., 2008. Composition, molecular structure, properties, and *in vitro* digestibility of starches from newly released Canadian pulse cultivars. Cereal Chemistry 85: 471-479.

Freitas, R.A., Paula, R.C., Feitosa, J.P.A., Rocha, S. and Sierakowski, M.R., 2004. Amylose contents, rheological properties and gelatinization kinetics of yam (*Dioscorea alata*) and cassava (*Manihot utilissima*) starches. Carbohydrate Polymers 55: 3-8.

Hsu, S., Lu, S. and Huang, C., 2000. Viscoelastic changes of rice starch suspensions during gelatinization. Journal of Food Science 65: 215-220.

Israkarn, K., Hongsprabhas, P. and Hongsprabhas, P., 2007. Influences of granule-associated proteins on physicochemical properties of mungbean and cassava starches. Carbohydrates Polymers 68: 314-322.

Jasim, A., 2012. Rheometric non-isothermal gelatinization kinetics of mung bean starch slurry: effect of salt and sugar. Journal of Food Engineering 109: 321-328.

Juliano, B.O. and Pérez, C.M., 1986. Kinetics studies on cooking of tropical milled rice. Food Chemistry 20: 97-102.

Keetels, C.J. and Van Vliet T.A.M., 1994. Gelation and retrogradation of concentrated starch gels. In: Lineback, D.R., Pillips, G.O., Williams, P.A. and Wedlock, D.J. (eds.) Gums and stabilizers for the food industry. IRL, New York, NY, USA, pp. 271-280.

Kim, Y. and Wang, S.S., 1999. Starch cooking with limited water as affected by zein and guar gum. Journal of Food Science 64: 133-135.

Kissinger, H.E., 1956. Reaction kinetics in differential thermal analysis. Analytical Chemistry 29: 1702-1706.

Malecki, A., Prochowska-Klisch, B. and Wojciechowski, K.T., 1998. Determination of the kinetics parameters of chemical reactions of the basis of non-isothermal measurement. Journal of Thermal Analysis and Calorimetry 54: 399-406.

Mendes da Silva, C.E., Ciacco, C.F., Barberis, G.E., Solano, W.M.R. and Rettori, C., 1996. Starch gelatinization measured by pulsed nuclear magnetic resonance. Cereal Chemistry 73: 297-301.

Murphy, P., 2000. Starch. In: Phillips, G.O. and Williams, P.A. (eds.) Handbook of hydrocolloids. Woodhead Publishing, Manchester, UK, pp. 46-66.

Ojeda, C.A., Tolaba, M.P. and Suarez, C., 2000. Modeling starch gelatinization kinetics of milled rice flour. Cereal Chemistry 77: 145-147.

Ozawa, T., 1970. Kinetic analysis of derivative curves in thermal analysis. Journal of Thermal Analysis 28: 301-324.

Okechukwu, P.E. and Rao, M.A., 1996. Kinetics of cowpea starch gelatinization based on granule swelling. Starch/Stärke 48: 43-47.

Pravisani, C.I., Califano, A.N. and Calvelo, A., 1985. Kinetics of starch gelatinization in potato. Journal of Food Science 50: 657-660.

Ratnayake, W.S. and Jackson, D.S., 2007. A new insight into the gelatinization process of native starches. Carbohydrate Polymers 67: 511-529.

Rhim, J.W., Nunes, R.V., Jones, V.A. and Swartsel, K.R., 1989. Determination of kinetic parameters using linearly increasing temperature. Journal of Food Science 54: 446-450.

Riva, M., Schiraldi, A. and Piazza, L., 1994. Characterization of rice cooking – isothermal differential scanning calorimetry investigations. Thermochimica Acta 246: 317-328.

Slade, L. and Levine, H., 1991. Critical reviews: beyond water activity – recent advances based on an alternative approach to the assessment of food quality and safety. Food Science Nutrition 30: 115-360.

Spigno, G. and Faveri, D.M., 2004. Gelatinization kinetics of rice starch studied by non-isothermal calorimetric technique: influence of extraction method, water concentration and heating rate. Journal of Food Engineering 62: 337-344.

Suzuki, K., Kubota, K., Omichi, M. and Hosaka, H., 1976. Kinetics studies on cooking rice. Journal of Food Science 41: 1180-1183.

Teyssandier, F., Cassagnau, P., Gérard, J.F., and Mignard, N., 2011. Sol-gel transition and gelatinization kinetics of wheat starch. Carbohydrate Polymers 83: 400-406.

Wunderlich, B. 1990. The advanced thermal analysis system, ATHAS. Shin Netsu Soku-teino Shinpo 1: 71-100.

Yañez-Farias, G.A., Moreno-Valencia, J.G., Del Refugio Falcón-Villa, M. and Barrón-Hoyos, J.M., 1997. Isolation and partial characterization of starches from dry beans (*Phaseolus vulgaris*) and chickpeas (*Cicer arietinum*), grown in Sonora, Mexico. Starch/Stärke 49: 341-345.

Yeh, A.L. and Li, J.Y., 1996. Kinetics of phase transition of native, cross-linked, and hydroxypropylated rice starches. Starch/Stärke 48: 17-21.

Yoon, W.B., Gunasekaran, J.W. and Park, S., 2004. Characterization of thermorheological behavior of Alaska pollock and pacific whiting surimi. Journal of Food Science 69: 338-343.

Zhang, X., Tong, Q., Zhu, W. and Ren, F., 2013. Pasting, rheological properties and gelatinization kinetics of tapioca starch with sucrose or glucose. Journal of Food Engineering 114: 255-261.

Zrinyi, M. and Horkay, F., 1987. On the elastic modulus of swollen gels. Polymer 28: 1139-1143.