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Full Length Research Paper

Hydrothermal characteristics of pearl millet (*Pennisetum glaucum*) flour during cooking into 'fura'

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The effects of hydration times (HT) (1, 3.5 and 6 h) and cooking times (CT) (20, 40, and 60 min) on the thermal characteristics of cooked pearl millet flour (CPMF) was investigated. The differential scanning calorimetry thermograms depicted two separate endothermic transitions identified as starch gelatinisation (29 to 30°C) and disruption of the starch-lipid complexes (90 to 120°C). The onset (T_o), peak (T_p) and completion temperature (T_c) of uncooked pearl millet flour (UPMF) were 50.6, 72.2 and 80.2°C respectively and that for the hydrated and CPMF ranged from 28.3 to 49.1°C, 47.9 to 79.7°C and 51.3 to 86.9°C respectively. The gelatinisation temperature range (ΔT_r) for the UPMF was 29.6°C and that of the treated flour ranged from 3.2 to 37.7°C. HT and CT significantly (P<0.05) affected the gelatinisation properties of the millet flour. HT gradually decreased the degree of gelatinisation, whereas, CT drastically increased the degree of gelatinisation. Hydrating millet flour for 1 h and cooking for 40 min was sufficient to achieve 100% gelatinised flour. Starch-lipid complex formed after gelatinisation at hydration time (3.5 h) and cooking for 40 min. HT (3.5 min) and CT (40 min) significantly decreased the T_o, T_p, T_c temperatures and uniformity of gelatinisation (PHI). The melting properties of the formed complex T_o, T_p and T_c of uncooked millet flour were 100.58, 118.58 and 135.21°C respectively while that for the hydrated and cooked millet flour ranged from 99.39 to 106.29, 114.79 to 119.02 and 133.07 to 137.01°C respectively. Melting range (ΔT_r) and melting enthalpy ($\Delta H_{melting}$), for the UPMF is 34.63°C and 1026.94 J/g respectively and 28.16 to 35.49°C, and 751.61 to 1072.44 J/g respectively for the CPMF. Increasing both the HT and CT reduced the amount of energy required to break the starch-lipid complex formed during the cooking of millet flour. The UPMF showed a typical A-type X-ray diffraction pattern, which was altered by the hydrothermal treatments (1 h hydration and 20 min cooking) resulting in a transformation into the V-hydrate form evidence of starch-lipid complex formation. The formation of this complex possibly explains why millet flour remains intact during cooking into fura.

Key words: Hydrothermal, fura, pearl millet flour, starch-lipid complexes, differential scanning calorimeter X-ray diffraction, complexing index.

INTRODUCTION

Hydrothermal treatment is the process of subjecting a food to elevated temperatures in the presence of moisture, whereby the physicochemical properties of the starch within the food are modified, without destroying the granule structure (Adebowale et al, 2005). The main hydrothermal treatments are annealing and heat-moisture treatments. Annealing (ANN) is the treatment of starch in excess water at temperatures below its gelatinisation temperature, while heat-moisture treatment (HMT) is the treatment of the starch at a lower moisture and higher temperature (Shih, 2007). During the course of this study, the hydrothermal treatment, annealing (ANN), would be expected to be the main focus, as the degree of gelatinisation of the cooked millet flour (CMF) would most likely be low at the core of the dumplings and extremely high on the surface. This is due to the fact that the core would be isolated from the heat of the boiling water. According to Shih (2007), starches are often

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characterised by differential scanning calorimetry (DSC) for gelatinisation transitions, and X-ray diffraction (XRD) for changes in crystalline status. The complexing index (CI) is used to determine the binding capacity of the starch for lipids, in order to investigate the starch-lipid complex formations. These complex formations take place immediately after gelatinisation in an exothermic process, as observed by DSC (De Phillí et al*.,* 2008). Before gelatinisation, the binding capacity of the starch for lipids is limited because most of the lipids in the system are unable to come into contact with the starch, as the starch is dispersed; the amylose becomes available for complexation (De Phillí et al*.,* 2008). Most application of pearl millet involve cooking, hence, the thermal properties that relate to its cooking quality should be studied.

Pearl millet (*Pennisetum glaucum*), which is also known as Bulrush millet, is the most widely grown type of millet. It is indigenous to Africa and was cultivated for domestic use about 4000 years ago (Anon, 2000). Pearl millet is a staple grain for about 90 million people living in the semi-arid tropical regions of Africa and the Indian sub-continent (Gulia et al*.,* 2007). Pearl millet flour can be used to make a semi-solid dumpling cereal meal, fura, a traditional porridge, common in West Africa. Fura is produced by mixing the millet flour with spices, like ginger and cloves, compressing into balls, and boiling for 30 min.

The cooked balls are then pounded to smooth, slightly elastic, cohesive dough while still hot. The dough is reshaped into smaller balls and dusted with flour to give the final product. Traditionally, fura is eaten by breaking the dough up and mixing it into yoghurt or buttermilk to form porridge (Jideani et al., 2002). During the boiling of the semi-solid dumplings, it is expected for the millet flour to disperse in the water since it contains no gluten (Taylor et al., 2006). However, the product remains intact during cooking and forms smooth, slightly elastic, cohesive dough (Jideani et al., 2002).

Production of fura involves boiling of the pearl millet flour. In general, heat effect on starchy foods results in gelatinisation of the starch, denaturation of proteins and complex formations between starch and lipids and between proteins and lipids (De Pilli et al., 2008). Some scientific research was carried out on pearl millet flour, such as the investigation of thermal treatments to prevent rancidity; however, no research into the hydrothermal properties of moist pearl millet flour during boiling has been reported. Furthermore, not much is known about the behaviour of pearl millet starch during cooking, and the effect of heat on pearl millet flour during processing into fura is not documented. Not much is known about the phenomena that keeps pearl millet flour intact during cooking.

The objective of this study was to characterise the thermal properties and gelatinisation transitions of pearl millet flour as affected by hydration and cooking times.

MATERIALS AND METHODS

Source of pearl millet flour

Pearl millet (*P. glaucum*) flour was obtained from Borolong Milling and Packaging (Botswana Marketing Board), Francistown, Botswana. The flour was sieved using a 710 micron sieve.

Nutritional analysis of pearl millet flour

Moisture, fat, protein and ash contents of the pearl millet flour were determined following the AOAC (2000) methods. Energy content (kJ/100 g) of pearl millet flour was estimated using the Atwater factor [(4 × protein) + (4 × carbohydrate) + (9 × fat)] × 4.2, where protein, carbohydrate and fat contents are expressed in g/100 g dry basis; 4, 4, and 9 are kilocalories from protein, carbohydrate, and fat respectively, while 4.2 is a factor for converting from calories to joules (Marero et al*.,* 1989). The determinations were carried out in triplicate.

Production of cooked pearl millet flour

The improved production process of fura as described by Jideani (2005) was used to produce the cooked pearl millet flour (CMF), as shown in Figure 1. Pearl millet flour (300 g), ginger (6 g) and cloves (1.5 g) were mixed thoroughly. Deionized water (142.5 ml) was mixed into the flour-spice mixture and left to hydrate for time (X_1) as determined in the design points outlined in Table 1. The hydrated flour was compressed between the palms of the hands, and dropped into 500 ml of boiling deionized water. The compressed flour was then cooked for time (X_2), according to the required cooking times outlined in the design points of Table 1. To stop further cooking, the cooked samples were immersed in ice water for 10 s and then dried with paper towel. The samples were then pounded slightly to break them open for easy drying of the samples. The cooked samples were dried for 16 h at 40°C using an oven drier. Once the CMF samples were dried, they were ground up to achieve a uniform sample. The samples were packaged in a plastic zip-lock bag and stored at freezing temperatures, until required for complexing index, thermal analysis and X-ray diffraction. The reference used for determining the complexing index of the CMF was cooked wheat flour (CWF), which was subjected to the same process methods as the CMF, including the various hydration times (X_1) and cooking times (X_2).

Experimental design

A 3^2 factorial experiment was used to study the effect of hydration time (X_1) and cooking time (X_2) on the hydrothermal characteristics of cooked pearl millet flour (CMF). Each of the factors was at three levels (Table 1). The numerical values were standardized to –1, 0, and +1. Nine experimental design points were carried out in a randomised order.

Complexing index of cooked pearl millet flour

The method of Gilbert and Spragg (1964) was used to determine the Complexing Index (CI) of the CMF. This was done by measuring the iodine binding capacity of the complex in relation to cooked wheat flour (CWF), as a reference. The iodine solution that was used in the analysis consisted of 2 g of potassium iodide and 1.3 g of I_2 in 50 ml of distilled water. The solution was left overnight, to completely dissolve and then made up to 100 ml in a volumetric

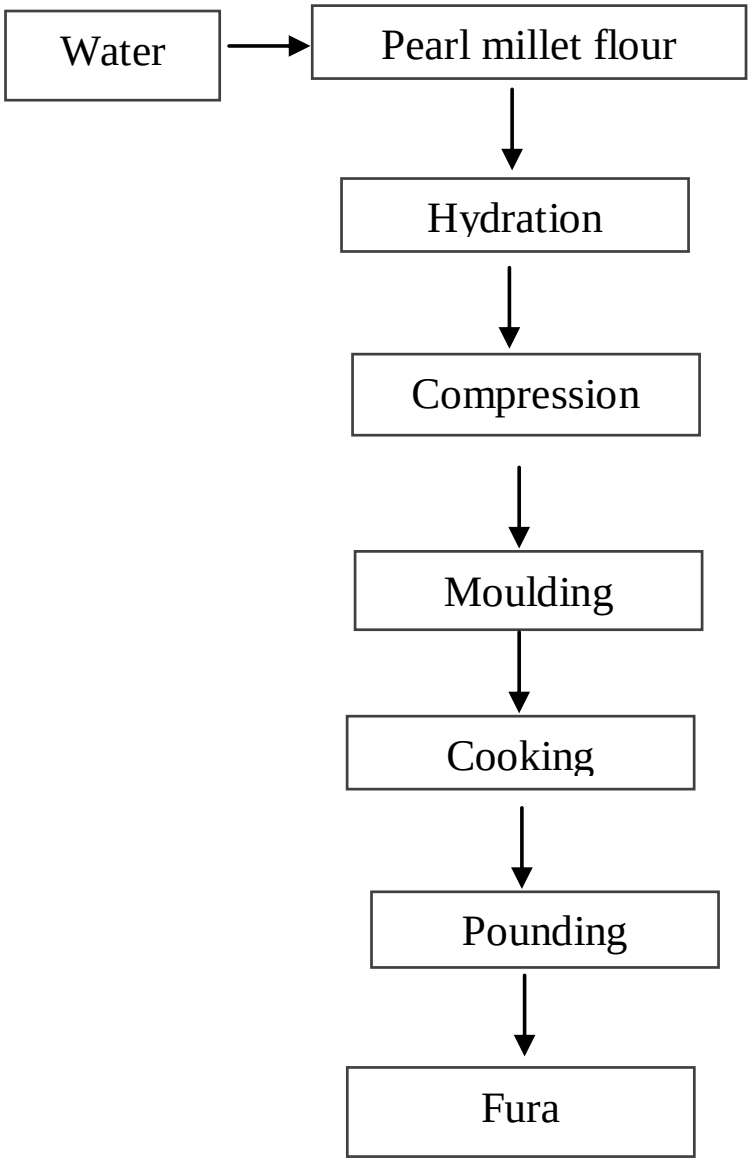


Figure 1. Improved fura production process (Jideani, 2005).

Table 1. Process variables and levels used of 3^2 factorial design*

Variable	Symbol	Coded variable level (*x*)		
		-1	0	+1
Hydration time (h)	X_1	1	3 ½	6
Cooking time (min)	X_2	20	40	60

*Transformation of coded variable (x_i) to uncoded variable (X_i) could be obtained from $X_1 = 2.5x_i + 3.5$; $X_2 = 20x_i + 40$.

flask using deionized water.

Samples (5 g) of CMF and CWF individually were placed in separate test tubes with 25 ml of distilled water, and mixed for 2 min, after which they were centrifuged for 15 min at 3000 rpm. Then, 500 µl of the supernatant was mixed with 15 ml of distilled water and 2 ml of the iodine solution. The tubes were then turned over three times and the absorbance of the samples measured at 690 nm using a UV-vis spectrophotometer. The CI was calculated using the following formula:

CI (%) = [(Abs reference – Abs starch-lipid) / Abs reference] × 100,

Table 2. Complexing characteristics of cooked millet flour as affected by hydration and cooking times.

Hydration time (h)	Complexing index (%)*			
Cooking time (min)	**20**	**40**	**60**	**Total**
1	63.2 ± 2.5	56.4 ± 9.3	17.3 ± 3.4	45.6 ± 22.0[a]
3.5	58.0 ± 7.8	60.0 ± 0.8	79.3 ± 1.3	65.8 ± 11.0[b]
6	37.9 ± 4.9	36.9 ± 9.4	6.3 ± 5.7	27.1 ± 16.7[c]
Total	53.0 ± 12.5[a]	51.1 ± 12.6[a]	34.3 ± 34.7[b]	

*Values are mean ± standard deviation. Values with different superscripts in the same column/row are significantly different at $P < 0.05$.

Where the Abs reference was the absorbance of CWF and Abs starch-lipid was the absorbance of CMF. The complexing index determination was done in triplicate.

Thermal analysis of cooked pearl millet flour

The degree of gelatinisation of the cooked pearl millet flour (CMF) and uncooked (control) were estimated using differential scanning calorimetry (DSC) following the method outlined by (Sozer et al*.,* 2007) with some modifications. Samples (40 mg) were placed into DSC pans, moistened with deionized water in a ratio of 2: 7, sealed and placed in a refrigerator at 4°C overnight to reach equilibrium. The next day, the samples were placed in the DSC and heated at a rate of 5°C/min from 30 to 140°C with nitrogen flushing at a rate of 20 cm^3/min. For each endotherm, onset (T_o), melting peak (T_p), and completion (T_c) temperatures were determined. The melting ranges ($\Delta T_r = T_c - T_o$) and the degree of gelatinisation (%) = [1 – ($\Delta H_t / \Delta H_s$)] × 100 were calculated, where ΔH_t is the gelatinisation enthalpy of the *CMF* at various cooking times (J/g db), and ΔH_s is the gelatinisation enthalpy of millet flour (J/g db).

Crystalline status of cooked pearl millet flour

The complex formation between the starch and lipids during hydrothermal treatments of the millet flour were examined using a Philips X-ray powder diffractometer (PW 3830 X-ray generator). The X-ray source was Cu Kα radiation, with a wavelength of 0.154056 nm. The X-ray diffractometer was operated in reflection mode at 40 kV and 30 mA. Data were collected over an angular range of 4 to 35°, using Phillips Software's X'Pert Data Collector to acquire the scans.

Data analysis

Analysis of variance (ANOVA) was used to determine the differences among the various hydrothermal treatments. The obtained parameter estimate effects were used to plot the response surface of the effects of hydration and cooking times. Duncan's multiple range tests was used to separate the means where significant differences exist. The statistical software SPSS v.16 (SPSS, 2007) was used.

RESULTS AND DISCUSSION

Proximate composition the millet flour

The proximate compositions of the pearl millet flour consisted of moisture (6.0 ± 0.27%), fat (8.1 ± 0.20%), protein (6.4 ± 0.4%), ash (1.7 ± 0.07%), carbohydrate (78.0 ± 0.4%) and energy (1722 ± 9 kJ/100 g). The fat content was significantly higher than values reported in the literature (5.0%) for pearl millet. The protein, ash and carbohydrate contents of the pearl millet flour were significantly less than those reported in the literature. The nutritional composition of cereals varies depending on their botanical origin (Shih et al*.,* 2007).

Complexing index

Complexing index is the measurement of the degree of starch-lipid complex formations. The fraction of the starch that is complexed to lipid will not bind to the iodine (De Phili et al., 2008). Hence, the absorbance reading was derived from the portion of starch that is complexed to the iodine. Table 2 gave details of the complexing characteristics of pearl millet flour as affected by hydration and cooking times. Cooking time, hydration time and their interaction significantly ($P<0.05$) affected the starch-lipid complexing characteristics of pearl millet flour with coefficient of determination at ($R^2 = 0.955$). The effects of hydration (1 and 3.5 h) and cooking (20 and 40 min) times on complexing index were significant at ($P<0.05$). The effect in both cases resulted to increase in starch-lipid complexing (Table 3). Hydration time (3.5 h) had a stronger effect (partial eta squared = 0.9278) on the starch-lipid complexing when compared with 1 h hydration time. Cooking times (20, 40 min) were both similar in their effects on starch-lipid complexing accounting for 70.7 and 69.3% of the variation in starch-lipid complex formation.

Hydrating the flour for 1 h and cooking for 20 or 40 min did not significantly affect the complex formation. However, hydration for 3.5 h and cooking for 30 to 40 min both significantly ($P<0.05$) imparted a positive effect on the formation of starch-lipid complex. Hydrating for 3.5 h and cooking for 60 min as well as, hydrating for 6 h and cooking for 20 to 60 min had a lesser effect on the complex formation. Furthermore, it has been reported that an increase in temperature results in a decreased

Table 3. Parameter estimates of the effect of hydration and cooking times on starch-lipid complexing in pearl millet flour.

Parameter	B	Std. error	t	Sig.	Partial eta squared
Intercept	6.31	3.39	1.86	0.0796	0.1609
(Hydration time = 1.0)	11.01	4.80	2.29	0.0340	0.2262
(Hydration time = 3.5)	73.04	4.80	15.21	0.0000	0.9278
(Hydration = 6.0)	0.00[a]	.	.	.	.
(Cooking time = 20)	31.63	4.80	6.59	0.0000	0.7069
(Cooking time = 40)	30.61	4.80	6.38	0.0000	0.6931
(Cooking time = 60]	0.00[a]	.	.	.	.
(Hydration time = 1.0) * (Cooking time=20)	14.27	6.79	2.10	0.0499	0.1971
(Hydration time = 1.0)* (Cooking time = 40)	8.46	6.79	1.25	0.2285	0.0795
(Hydration time = 1.0) * (Cooking time = 60)	0.00[a]	.	.	.	.
(Hydration time = 3.5) * (Cooking time = 20)	-52.97	6.79	-7.80	0.0000	0.7718
(Hydration time = 3.5) * (Cooking time = 40)	-49.96	6.79	-7.36	0.0000	0.7505
(Hydration time = 3.5] * (Cooking time = 60)	0.00[a]	.	.	.	.
(Hydration time = 6.0] * (Cooking time = 20)	0.00[a]	.	.	.	.
(Hydration time = 6.0)* (Cooking time = 40)	0.00[a]	.	.	.	.
(Hydration time = 6.0) * (Cooking time = 60)	0.00[a]	.	.	.	.

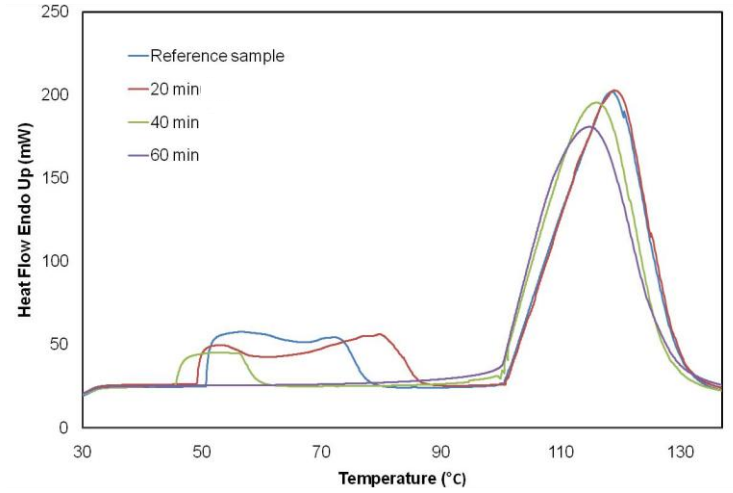
[a] This parameter is set to zero because it is redundant.

swelling power that has been attributed to an increased complex formation (Gray and Schoch, 1962). However, for extrusion processes, an optimum temperature above and below which a decrease in lipid binding occurs has been reported (Bhatnagar and Hanna, 1994 a, b; De Pilli et al., 2008). Starch-lipid complex was maximum at hydration and cooking time of 3.5 h and 40 min, respectively. Complex formation was reported to have taken place immediately after gelatinisation in an exothermic process (Kugimiya et al., 1980). According to De Pilli et al. (2008), starch binding capacity for lipid before gelatinisation is limited because most of the lipid in the system was unable to come into contact with the starch. Hydration time (3.5 h) explaining 92.8% of the variability in starch-lipid complexing suggests that starch-lipid complexing occurred during hydration.

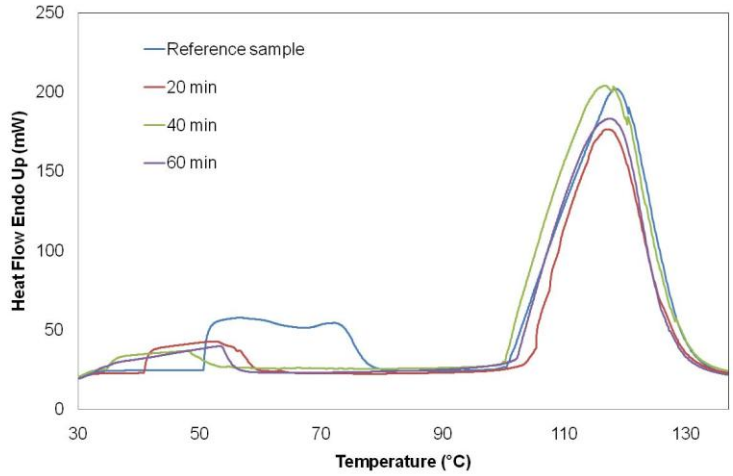
Thermal characteristics of cooked pearl millet flour

The endothermic transitions from raw and cooked pearl millet flour as affected by hydration and cooking times are shown in Figure 2. Two endothermic peaks were observed and attributed respectively to starch gelatinisation (Chung et al*.,* 2008a), toward the peak of the curve and starch-lipid complex formation by an exothermic process as the curve returns to the rest position (Kugimiya et al*.,* 1980). The second peak, a much larger one in the higher temperature region of the thermogram, with peaks between 90 and 120°C represents the melting or disruption of the starch-lipid complexes formed previously (Chung et al*.,* 2008a). Gelatinisation of starch molecules within food is a very important phenomenon that occurs during numerous food processing operations. Its importance lies in its ability to provide unique structural and textural properties within the product (Sozer et al., 2007). During the processing of fura, millet flour was subjected to various hydrothermal treatments by investigating the kinetics of starch gelatinisation behind these treatments so that the effect of, and optimal conditions for thermal processing of millet flour can be drawn (Spingo and De Faveri, 2004). The gelatinisation temperatures (onset, T_o, peak, T_p, and completion, T_c), gelatinisation temperature range (ΔT_r), enthalpy of gelatinisation (ΔH_{gel}) and Peak Height Index (PHI) for uncooked and cooked millet flour as affected by hydration and cooking times was measured using differential scanning calorimeter as presented in Table 4. The onset, peak and completion temperature of uncooked millet flour were 50.6, 72.2 and 80.2°C respectively while that for the hydrated and cooked millet flour ranged from 28.3 to 49.1°C, 47.9 to 79.7°C and 51.3 to 86.9°C respectively.

The gelatinisation temperature range (T_c-T_o) for the uncooked and treated flour were 29.6°C and 3.2 to 37.7°C respectively. Reported gelatinisation temperature ranges (T_r) for other cereal and legume flours was around 10 to 15°C (Sozer et al., 2007) while other starches range between 18 to 25°C (Chung et al., 2008b). The gelatinisation temperature range for millet flour on the other hand looking at the unprocessed flour was around 29 to 30°C, which is similar to that of rice starch ranging



(A)



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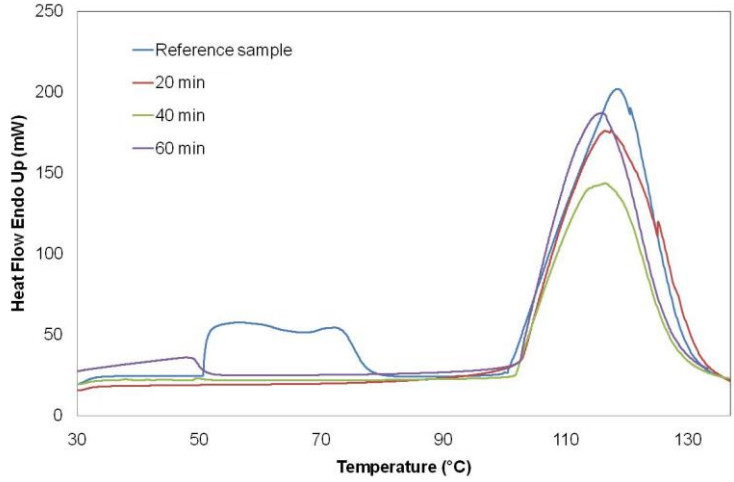

(C)

Figure 2. DSC thermograms for CMF at (A) 1.0 h, (B) 3.5 h, (C) 6.0 h hydration and various cooking times.

Table 4. Gelatinisation properties of cooked pearl millet flour as affected by hydration and cooking time.

Samples	Cooking time (min)	Temperature (°C)				Δ*H* (J/g)	Degree of gelatinisation (%)	PHI
		T_o (°C)	T_p (°C)	T_c (°C)	ΔT_r (°C)			
Reference	0	50.62 ± 0.13[a]	72.20 ± 0.16[a]	80.20 ± 0.17[a]	29.578 ± 0.05[a]	397.227 ± 0.02[a]	nd	18.4 ± 0.01[a]
1 h Hydration	20	49.12 ± 0.09[b]	79.70 ± 0.11[b]	86.86 ± 0.11[b]	37.74 ± 0.05[b]	463.43 ± 0.01[b]	0.00	15.2 ± 0.01[b]
	40	45.56 ± 0.10[c]	52.91 ± 0.12[c]	59.85 ± 0.13[c]	14.29 ± 0.03[c]	162.93 ± 0.06[c]	58.98 ± 0.02[c]	22.2 ± 0.06[c]
	60	nd	nd	nd	nd	nd	nd	nd
3.5 h Hydration	20	40.84 ± 0.10[d]	52.20 ± 0.12[d]	59.55 ± 0.12[d]	18.71 ± 0.04[d]	188.18 ± 0.05[d]	52.63 ± 0.02[d]	16.6 ± 0.03[d]
	40	34.64 ± 0.11[e]	48.00 ± 0.12[e]	52.52 ± 0.11[e]	17.88 ± 0.02[e]	160.08 ± 0.08[e]	59.70 ± 0.03[e]	12.0 ± 0.001[e]
	60	32.47 ± 0.11[f]	53.28 ± 0.11[f]	56.42 ± 0.11[f]	23.95 ± 0.01[f]	206.36 ± 0.08[f]	48.05 ± 0.03[f]	9.9 ± 0.004[f]
6 h Hydration	20	nd	nd	nd	nd		nd	nd
	40	48.88 ± 0.11[g]	49.69 ± 0.11[g]	52.04 ± 0.12[g]	3.16 ± 0.01[g]	19.85 ± 0.01[g]	95.00[g]	24.5 ± 0.02[g]
	60	28.19 ± 0.24[h]	47.88 ± 0.11[h]	51.31 ± 0.11[h]	23.03 ± 0.01[h]	197.08 ± 0.07[h]	50.39 ± 0.03[h]	10.1 ± 0.07[h]

Values are mean ± standard deviation; Values followed by a different superscript in each column are significantly different ($P < 0.05$); hydration and cooking times: onset (T_o), peak (T_p), and completion (T_c) temperatures, gelatinization enthalpies (Δ*H*), and gelatinization ranges (Δ$T_r = T_c - T_o$); nd = not detected.

from 26 to 31°C (Shih et al., 2007). The large gelatinisation temperature ranges are most probably due to crystallites of contrasting stability within the crystalline domains of the starch molecules (Singh et al., 2004).

The gelatinisation temperatures of uncooked flour significantly ($P < 0.05$) differed from that of the hydrated and cooked flour. Onset temperature of uncooked flour was significantly ($P<0.05$) higher than those of the hydrated and cooked flours. The higher onset temperature for uncooked flour indicated that more energy is required to initiate starch gelatinisation from uncooked flour when compared to hydrated flour. Generally, the completion temperature (T_c) increases with the protein content and melting enthalpy of starch-lipid complexes (Liu et al., 2007). For cereal grains, the value is usually around 65 to 70°C (Sozer et al., 2007). The completion temperature of the unprocessed millet flour was around 80°C. However, the protein content of millet was only 6.4% compared to that of other cereal grains ranging between 10 to 15% protein (Sozer et al., 2007). This implies that the tremendously high melting enthalpy of the starch-lipid complexes visible by the large peaks in the higher temperature ranges of the thermograms are responsible for the high completion temperatures of the millet flour despite the low protein content. Gelatinisation temperatures are greatly affected by four main properties within the structure of a product namely; protein content, starch structure (Kaur and Singh, 2005), melting enthalpy of starch-lipid complexes and protein-starch interactions (Liu et al., 2007). Increase in starch-lipid complex formations decreases the extent of hydration in the amorphous areas, thus, resulting in an increased amount of thermal energy required for melting (Jayakody et al., 2005). The high fat content of millet flour (8.1%) is directly related to the formation of starch-lipid complexes. A similar trend had been reported for chickpea flour whose fat content was similar to that of millet flour, with its T_c values for starch-lipid complex disruption much higher compared to those of other flours (Chung et al., 2008b).

Hydration and cooking times significantly ($P<0.05$) affected the gelatinisation properties of the millet flour. Parameter estimates of the effects (Table 5) indicated that the main effects hydration times (1.0 and 3.5 h) and cooking times (20 and 40 min) had the significant effects compared to the effects of hydration time (6 h) and cooking time (60 min). Hydrating millet flour for 1 h had a positive effect on all the gelatinisation temperatures except for T_o, and PHI. Hydrating millet flour for 3.5 h affected the gelatinisation

Table 5. Parameter estimates for the effect of hydration and cooking times on gelatinisation temperatures of millet flour.

Dependent variable[a]	Parameter estimate (B)						
	Temperature (°C)				ΔH_{gel} (J/g)	Degree of gelatinisation (%)	PHI (J/g/°C)
	T_o	T_p	T_c	ΔT_r			
Intercept	28.19	47.88	51.31	23.12	197.08	50.39	10.01
(Hydration time = 1.0)	-3.32	3.22	7.81	11.12	143.08	-36.02	-2.35
(Hydration time = 3.5)	4.28	5.40	5.11	0.83	9.28	-2.34	-0.09
(Hydration time = 6.0)	0.00[b]	0.00[b]	0.00[b]	0.00[b]	0.00[b]	0[b]	0.00[b]
(Cooking time = 20)	8.37	-1.08	3.14	-5.23	-18.18	4.58	6.64
(Cooking time = 40)	20.69	1.81	0.74	-19.95	-177.23	44.62	14.50
(Cooking time = 60)	0.00[b]	0.00[b]	0.00[b]	0.00[b]	0.00[b]	0[b]	0.00[b]
(Hydration time = 1.0) * (Cooking time = 20)	15.89	29.67	24.61	8.73	141.45	-18.94	0.86
(Hydration time = 1.0) * (Cooking time = 40)	0.00[b]	0.00[b]	0.00[b]	0.00[b]	0.00[b]	0[b]	0.00[b]
(Hydration time = 1.0) * (Cooking time = 60)	0.00[b]	0.00[b]	0.00[b]	0.00[b]	0.00[b]	0.00[b]	0.00[b]
(Hydration time = 3.5) * (Cooking time = 20)	0.00[b]	0.00[b]	0.00[b]	0.00[b]	0.00[b]	0[b]	0.00[b]
(Hydration time = 3.5) * (Cooking time = 40)	-18.52	-7.09	-4.64	13.88	130.94	-32.97	-12.44
(Hydration time = 3.5) * (Cooking time = 60)	0.00[b]	0.00[b]	0.00[b]	0.00[b]	0.00[b]	0.00[b]	0.00[b]
(Hydration time = 6.0) * (Cooking time = 20)	0.00[b]	0.00[b]	0.00[b]	0.00[b]	0.00[b]	0.00[b]	0.00[b]
(Hydration time = 6.0) * (Cooking time = 40)	0.00[b]	0.00[b]	0.00[b]	0.00[b]	0.00[b]	0.00[b]	0.00[b]
(Hydration time = 6.0) * (Cooking time = 60)	0.00[b]	0.00[b]	0.00[b]	0.00[b]	0.00[b]	0.00[b]	0.00[b]

[a] $P<0.05$ with partial eta squared > 0.800, [b] This parameter is set to zero because it is redundant. T_o = onset temperature; T_p = peak temperature; T_c = completion temperature; ΔT_r = gelatinization range ($T_c - T_o$); ΔH_{gel} = enthalpy of gelatinisation; PHI = peak height index = $\Delta H_{gel}/ (T_p - T_o)$.

temperatures positively except for degree of gelatinisation and PHI where its effect was negative. Thus, increasing hydration time significantly decreased the energy required to initiate gelatinisation and decreases uniformity in gelatinisation. This may be due to the difference in granule structures (Singh and Singh, 2001) as the starch absorbs moisture. Cooking millet flour for 20 min positively affected T_o, T_c, and PHI while negatively affecting T_p, ΔT_r and ΔH_{gel}. Cooking millet flour for 40 min positively affected all the gelatinisation temperatures except for ΔT_r and ΔH_{gel} where the effect was negative. Thus, increasing cooking time decreases the range of gelatinisation and the energy required to initiate gelatinisation while improving the uniformity in gelatinisation. With the beginning of gelatinisation, starch granules become less thermostable and less energy is required to melt its structure (Biliaderis and Zawistowski, 1990). The lack of gelatinisation endotherm for 60 min cooking means that the sample was completely gelatinised (Sozer et al., 2007).

Interaction between hydration and cooking times significantly ($P<0.05$) affected the gelatinisation temperatures of millet flour. Parameter estimates of the effects (Table 5) indicated that the interaction effects of hydration time (1.0 h)*, cooking time (20 min); hydration time (3.5 h)* and cooking time (40 min) had significant effects. The effect of hydration time (1 h)* and cooking time (20 min) was positive on all the gelatinisation temperatures. Hydrating the flour for 3.5 min and cooking for 40 min significantly decreased the onset-, peak-, completion temperatures and uniformity of gelatinisation.

Effect of hydration and cooking times on the degree of gelatinisation are shown in Figure 3. Hydration significantly decreased the degree of gelatinisation while cooking time drastically increased the degree of gelatinisation. Hydrating (1 h) and cooking for 40 min was

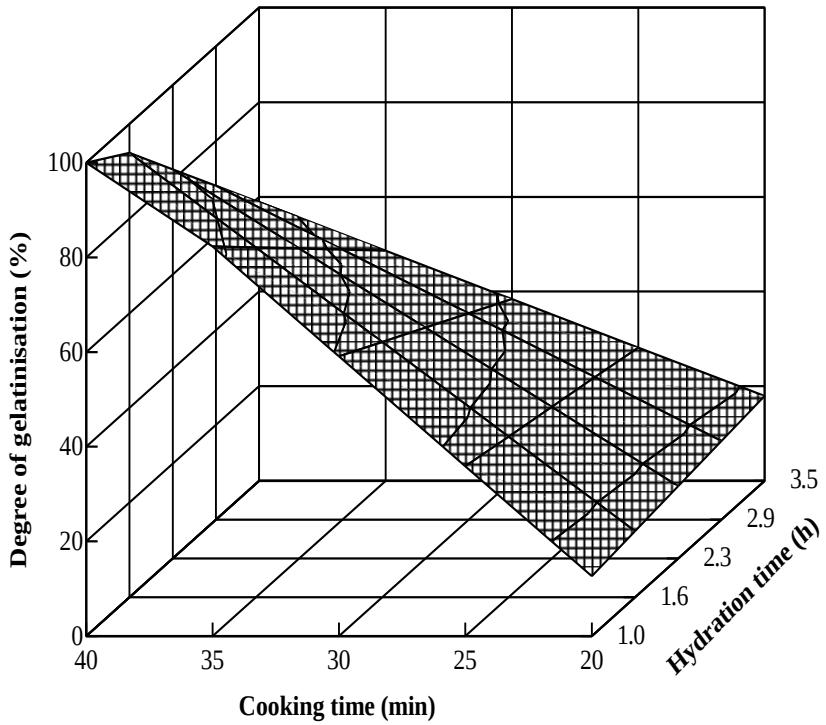

Figure 3. Effects of hydration and cooking times on the degree of gelatinisation of pearl millet flour.

Table 6. Thermal properties of cooked pearl millet at various hydration and cooking times.

Samples	Cooking time (min)	Temperature (°C)*				Δ*H* (J/g)
		T_o	T_p	T_c	ΔT_r	
Reference	0	100.58 ± 0.16	118.58 ± 0.17	135.21 ± 0.17	34.630 ± 0.01	1026.940 ± 0.08
1 h Hydration	20	106.29 ± 0.14	119.02 ± 0.16	134.45 ± 0.18	28.16 ± 0.04	999.838 ± 0.03
	40	100.38 ± 0.13	116.07 ± 0.17	133.21 ± 0.17	32.83 ± 0.04	1027.841 ± 0.22
	60	99.39 ± 0.16	114.79 ± 0.16	133.83 ± 0.17	34.44 ± 0.02	943.613 ± 0.25
3.5 h Hydration	20	104.95 ± 0.16	117.19 ± 0.17	133.54 ± 0.17	28.59 ± 0.01	781.346 ± 0.07
	40	100.19 ± 0.15	116.75 ± 0.15	134.27 ± 0.17	34.08 ± 0.02	1072.441 ± 0.05
	60	101.42 ± 0.16	117.51 ± 0.17	133.07 ± 0.17	31.65 ± 0.02	863.558 ± 0.21
6 h Hydration	20	101.52 ± 0.16	117.49 ± 0.17	137.01 ± 0.17	35.49 ± 0.01	952.574 ± 0.40
	40	100.79 ± 0.17	116.62 ± 0.16	135.46 ± 0.17	34.67 ± 0.01	751.611 ± 0.06
	60	102.25 ± 0.17	115.95 ± 0.17	133.36 ± 0.17	31.11 ± 0.01	908.881 ± 0.11

*T_o = onset temperature; T_p = peak temperature; T_c = completion temperature; ΔT_r = gelatinization range ($T_c - T_o$); ΔH_{gel} = enthalpy of gelatinisation.

sufficient to achieve 100% gelatinised millet flour.

Melting characteristics of pearl millet flour as affected by hydration and cooking times

Table 6 shows the thermal properties of cooked millet flour (T_o, T_p and T_c) and melting enthalpies (Δ*H*), with respect to disruption of the starch-lipid complexes formed during the exothermic rebate section of the thermogram after the gelatinisation peak. The peak melting temperature (T_p) for the uncooked pearl millet flour was 118.58°C, while the peak melting temperatures of the cooked pearl millet flour ranged from 114.79 to 119.02°C.

Table 7. Parameter estimates for the effect of hydration and cooking times on thermal properties of cooked pearl millet.

Dependent variable[a]	Temperature (°C)				$\Delta H_{melting}$ (J/g)	PHI (J/g/°C)
	T_o	T_p	T_c	ΔT_r		
Intercept	102.50	115.95	133.36	30.85	908.88	67.60
(Hydration time = 1.0)	-3.11	-1.16	0.47	3.59	34.73	-6.33
(Hydration time = 3.5)	-1.08	1.57	-0.29	0.80	-45.32	-13.95
(Hydration time = 6.0)	0.00a	0.00[a]	0.00[a]	0.00[a]	0.00a	0.00a
(Cooking time = 20)	-0.98	1.54	3.65	4.64	43.69	-7.95
(Cooking time = 40)	-1.71	0.67	2.11	3.82	-157.28	-20.12
(Cooking time = 60)	0.00[a]	0.00[a]	0.00[a]	0.00a	0.00[a]	0.00[a]
(Hydration time = 1.0) * (Cooking time = 20)	7.88	2.78	-3.03	-10.92	12.54	24.67
(Hydration time = 1.0) * (Cooking time = 40)	2.63	0.61	-2.73	-5.36	241.51	24.04
(Hydration time = 1.0) * (Cooking time = 60)	0.00[a]	0.00[a]	0.00[a]	0.00[a]	0.00a	0.00[a]
(Hydration time = 3.5) * (Cooking time = 20)	4.51	-1.87	-3.18	-7.70	-125.90	18.14
(Hydration time = 3.5) * (Cooking time = 40)	0.49	-1.44	-0.91	-1.40	366.15	31.25
(Hydration time = 3.5) * (Cooking time = 60)	0.00[a]	0.00[a]	0.00[a]	0.00[a]	0.00[a]	0.00[a]
(Hydration time = 6.0) * (Cooking time = 20)	0.00[a]	0.00[a]	0.00[a]	0.00[a]	0.00[a]	0.00[a]
(Hydration time = 6.0) * (Cooking time = 40)	0.00[a]	0.00[a]	0.00[a]	0.00[a]	0.00[a]	0.00[a]
(Hydration time = 6.0) * (Cooking time = 60)	0.00[a]	0.00[a]	0.00[a]	0.00[a]	0.00[a]	0.00[a]

[a] $P<0.05$ with partial eta squared > 0.800, [b] This parameter is set to zero because it is redundant. T_o = onset temperature; T_p = peak temperature; T_c = completion temperature; ΔT_r = gelatinization range ($T_c - T_o$); ΔH_{gel} = enthalpy of gelatinisation; PHI = peak height index = $\Delta H_{gel}/ (T_p - T_o)$.

The onset temperature (T_o) for the uncooked pearl millet flour was 100.58°C, while that of the cooked millet flour range from 99.39 to 106.29°C. The completion temperature (T_c) for uncooked pearl millet flour was 135.21°C, whereas the completion temperatures of the cooked pearl millet flour ranged from 133.07 to 137.01°C. Melting range and melting enthalpy for the uncooked pearl millet flour was 34.63°C and 1026.94 J/g respectively, while the melting ranges and melting enthalpies of the cooked pearl millet flour ranged from 28.16 to 35.49°C, and 751.61 to 1072.44 J/g respectively. Hydration and cooking times affected the melting properties of the millet flour significantly ($P < 0.05$). Parameter estimates of the effects (Table 7) indicated that main effects of hydration times (1.0 and 3.5 h) and cooking times (20 and 40 min) were significant when compared to the effects of hydration time (6 h) and cooking time (60 h). The main effect of hydrating the millet flour for 1 h was negative on onset and peak temperatures. The main effect of hydrating the millet flour for 3.5 h was negative for T_o, T_c and $\Delta H_{melting}$. Generally, the effect of hydration was a decrease on T_o, T_p, and $\Delta H_{melting}$ temperatures but an increase on T_c and T_r range. Shih et al. (2007) reported that hydration increases the onset (T_o), peak (T_p) and completion temperatures (T_c) and results in a thinner gelatinisation peak (T_r). Hydration was found to decrease the T_o, T_p and $\Delta H_{melting}$ while increasing the T_c and T_r.

The main effect of cooking millet flour for 20 min negatively affected the T_o. Cooking for 40 min negatively affected T_o and $\Delta H_{melting.}$ Hydrating for 1 h and cooking for either 20 min or 40 min negatively affected T_c and ΔT_r. Hydrating for 3.5 h and cooking for 20 min negatively affected all the properties except T_o where its effect was positive and cooking for 40 min at this hydration time negatively affected Tp, Tc and ΔT_r. Cooking generally decreased T_o and $\Delta H_{melting}$ while increasing T_c, T_r and T_p. However, Sozer et al. (2007) reported that T_o values were increased as cooking time progressed. Increasing both the hydration and cooking times reduced the amount of energy required to break the starch-lipid complex formed during the cooking of millet flour.

Effect of hydration and cooking times on the crystalline structure of pearl millet flour

X-ray diffraction was used in the study to attain qualitative evidence of the formation of starch-lipid complexes. The powder X-ray diffractograms of the uncooked, un-hydrated pearl millet flour control sample is shown in Figure 4. The X-ray diffraction pattern of the uncooked pearl millet flour showed peaks at 2θ values of 15.5, 18.5 and 23.5° resembling an A-type X-ray diffraction pattern, with peaks at typical for cereal starches (Zobel, 1988). According to Jenkins et al. (1993), the A-type pattern is as a result of the formation of double helical structures of the amylopectin fraction. The crystalline structure of the starch was preserved by the lipids present in the product (Guy, 1994), which is directly related to its fat content.

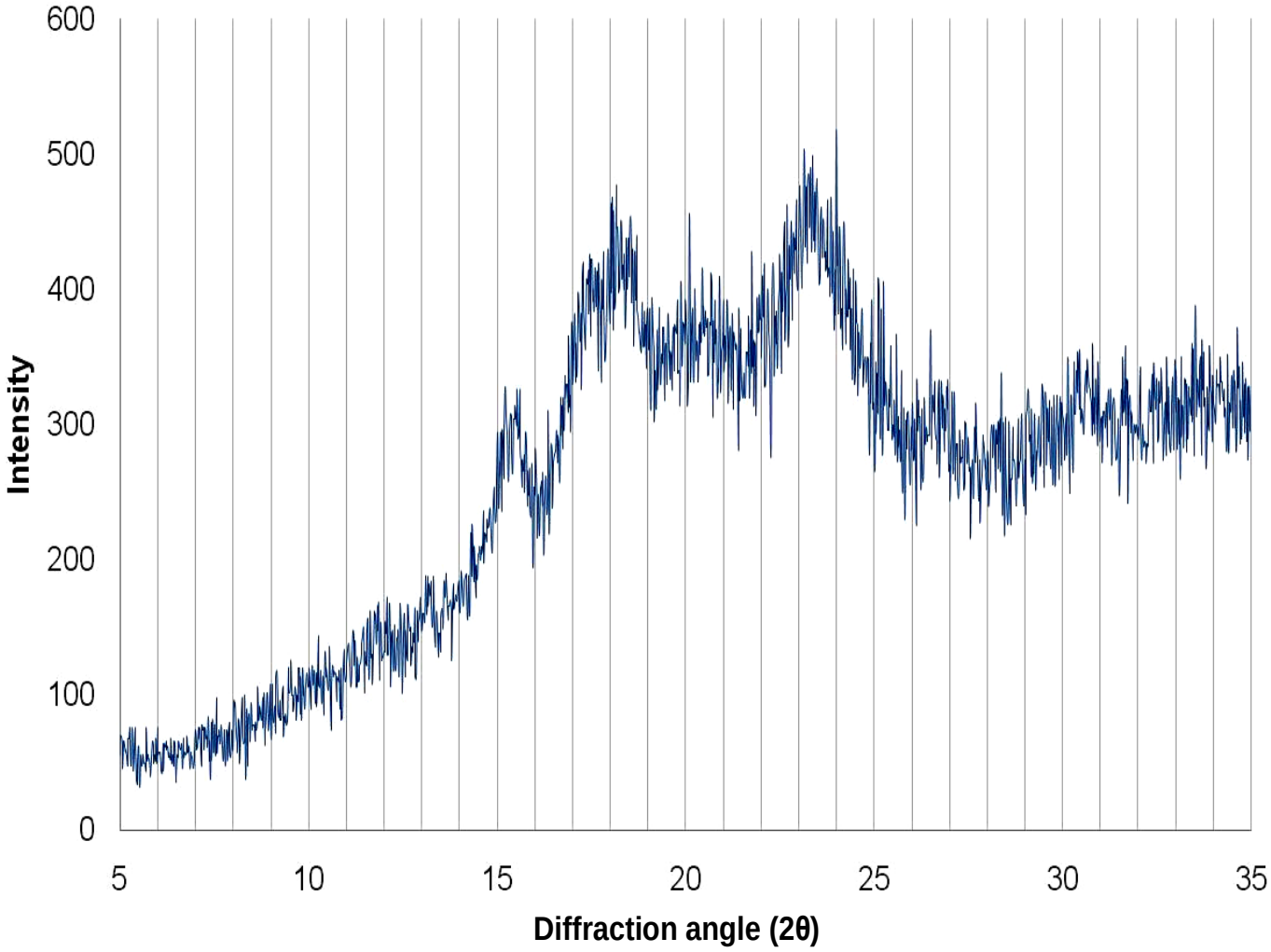

Figure 4. XRD pattern of uncooked pearl millet flour (*Pennisetum glaucum*).

Effects of hydration and cooking times on the XRD patterns of millet flour are shown in Figure 5. Upon hydrating of the flour for 1 h and cooking for 20 min, the X-ray diffraction pattern changed to V-hydrate form characterized by peaks at 17.5 and 20.0° 2θ. The development of this pattern suggests the possible formation of amylose-lipid complexes (Shih et al., 2007) of hydrated and cooked millet flour. This was reported for heat-treated rice starch under severe parboiling conditions (Derycke et al., 2005) and for extruded blend of wheat and almond flours at barrel temperature more than 90°C (De Phili et al., 2008).

The basic shape of the XRD pattern was maintained with decreased intensity but well defined peaks as cooking time increased. A decrease in intensity can be either as a result of crystalline disruption or reorientation of the double-helix pairs forming the array (Perera et al., 1997). In general, the decrease in endothermic transitions observed by DSC was related to the loss of crystalline structure as seen by the X-ray diffractograms (Zobel, 1988).

Conclusions

DSC gelatinisation endotherms decreased in magnitude as the hydration time and cooking time increased, which is a possible indication of the formation of starch-lipid complexes. However, at extended cooking times, disruption of these complexes was evident. Overall, the XRD patterns showed that the native pearl millet flour (*P. glaucum*) had the characteristic A-type pattern of the cereal starches. With an increase in hydration time, this A-type pattern was transformed into the V-hydrate form, while during an increase in cooking time; the XRD pattern retained its characteristic shape, though, with lower intensities. Furthermore, it was once again evident that extended cooking times had a negative effect on the

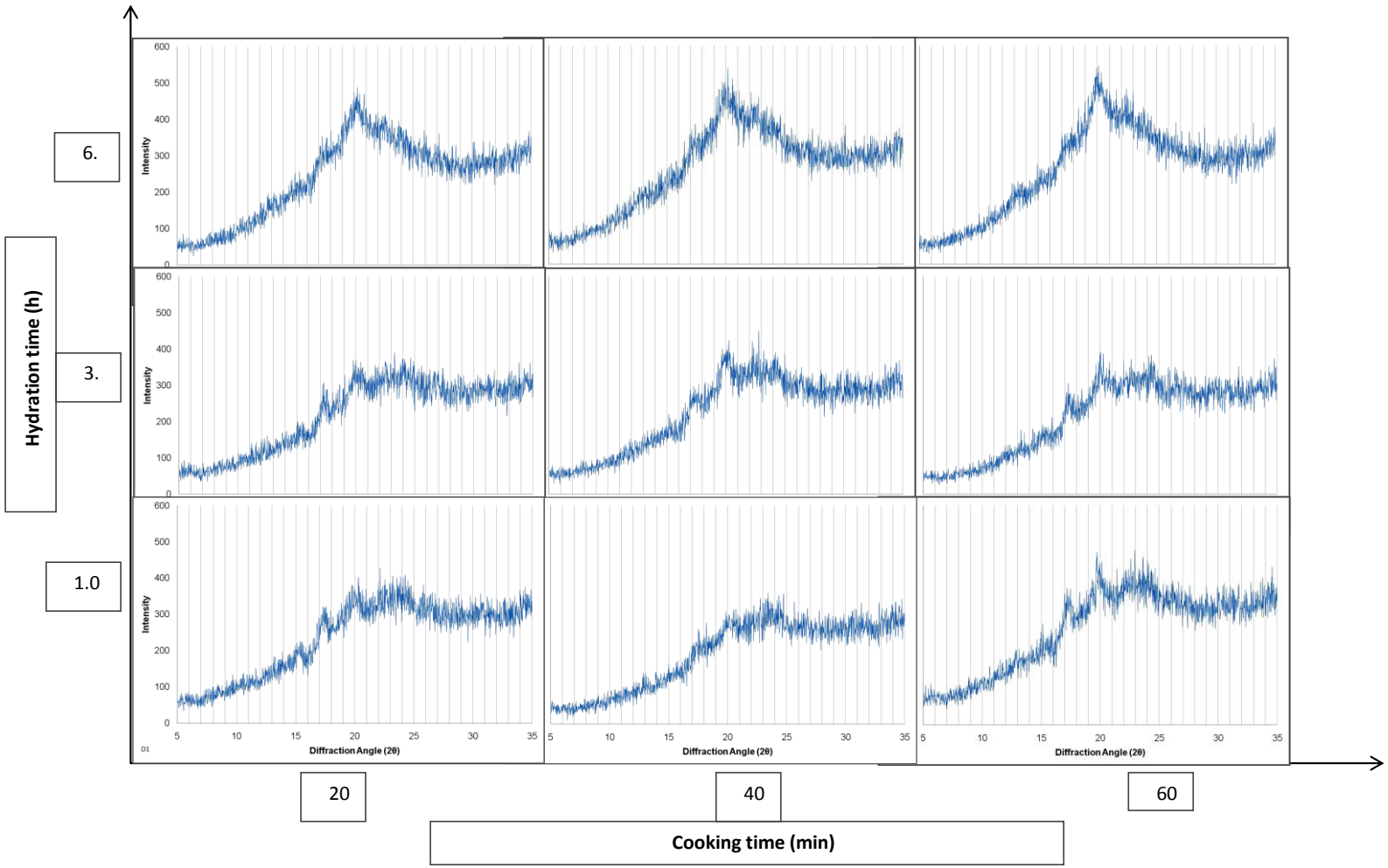

Figure 5. Effect of hydration and cooking times on the crystalline structure of pearl millet flour.

formation of starch-lipid complexes. Results for complexing index were evident of the formation of starch-lipid complexes and the trends seen in these results supported those found during the DSC analysis.

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