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Variation in nutrient composition and structure of high-moisture maize dried at different temperatures

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Abstract

Maize cobs with grains were harvested at a relatively high moisture content (23%) from the field in northern New South Wales, Australia. The cobs were divided into four categories and dried in the sun or artificially in a forced draft oven at 80, 90 or 100 °C for 24 h. The samples were subjected to proximate and detailed nutrient analyses. *In vitro* nutrient digestibility and ultra structure of samples were also assessed. Proximate analysis of maize revealed that dry matter (DM, 980 g/kg) and ash (1.32 g/kg) content were highest in the 100 °C samples, but crude protein (98.4 g/kg), ether extract (45.0 g/kg) and phytate–P (1.8 g/kg) content were the highest in the sundried samples. Gross energy was little affected by heat treatment but the metabolizable energy value increased with rising temperature. The concentrations of most of the amino acids but not lysine were increased in samples dried at 80, 90 and 100 °C in comparison to sun drying. Total starch, resistant starch (RS) and amylose content were slightly increased by artificial drying while amylopectin was reduced under the same conditions. Starch content (691 g/kg) was highest at 80 °C while RS (363 g/kg) and amylose (304 g/k) were lowest in the same batch. The mineral concentration of samples decreased with increasing temperature except copper, which was slightly increased. The soluble non-starch polysaccharide (NSP) content was increased while the insoluble NSP decreased with increasing temperature. The morphological structure of maize observed under a scanning electron microscope showed some shrinkage of starch granules as a consequence of artificial drying temperature. *In vitro* digestibility of DM was improved as a result of artificial drying of high moisture maize but starch digestibility was reduced. It may be inferred that the nutritive value of maize grain varies with drying temperature and drying process. These differences may explain changes in nutritive value of the grain when fed to chickens.

Keywords: Maize, drying temperature, composition, structure
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Introduction

Maize (*Zea mays*) is used as a principal energy source for intensive animal industries throughout the world. It is usually harvested at a relatively high moisture (HM) content to minimize damage in the field when left to dry naturally. In many countries, including Australia, maize is usually harvested either with high moisture content to minimize damage in the field or kept in the field for an extended period of time to dry naturally before harvesting. High moisture maize is then subjected to artificial drying before milling for animal feeding. This artificial drying may result in loss of quality such as an increase in the retrograde starch (resistant starch type 3; RS3) content (Brown, 1996). Retrograde starch is caused by high temperature heating of grains followed by storage at low temperature. Heat processing may also anneal the starch as the grains cool down. Improper natural or artificial drying has been linked to decreased starch yield, increased stress cracking and kernel breakage (Peplinski *et al.*, 1994). The digestibility of cereal grains is influenced by the starch component, especially the ratio between amylose and amylopectin (McDonald *et al.*, 1995). Due to the amorphous nature of amylopectin it is more readily digested than amylose.

The normal structure of starch granules from maize (spherical, 10 - 16 microns across) with protein bodies and matrix creates a favourable environment for enzymatic digestion (Taylor & Belton, 2002). This structure may be altered after artificial drying of HM grains, which may affect the nutritive value. There is a report that the crude protein of stack-burned yellow maize does not change much due to high temperature drying. However, there was a reduction in concentrations of various amino acids, an increase in Maillard reaction products and a reduction in *in vitro* digestibility due to such treatment (Panigrahi *et al.*, 1996).

The present study was carried out to investigate the effect of artificial drying of HM maize on the chemical composition and ultra-structure of the maize grains as well as the *in vitro* digestibility of the grains.

Materials and Methods

Maize grain from the 2009 planting year (at the end of April), was obtained from Inverrel in northern New South Wales, Australia, and contained *ca*. 23% moisture. After collection, the cobs were split into four groups. The first group was dried in the sun for three days until the moisture content dropped to a constant level of about 13%. The other three groups were dried artificially using a forced draft oven at 80, 90 or 100 °C for 24 h. After the drying process, the warm samples were placed in paper bags and cooled at room temperature overnight. Upon cooling, the cobs were threshed with a manual corn sheller. Samples of all batches were ground with a hammer mill to pass through a 1 mm mesh screen and stored at 4 °C until analyses.

The proximate nutrient composition of the samples was measured in duplicate using standard AOAC (2002) methods. Metabolizable energy (ME) was calculated according to the equation:

$$\text{ME (Kcal/kg)} = 53+38 \times (\%\text{CP} + 2.25 \times \%\text{EE} + 1.1 \times \%\text{Starch} + \%\text{Sugar})$$

where CP is crude protein and EE is ether extract (Carpenter & Clegg, 1956). The values were converted to MJ/kg using a conversion factor of 1 MJ = 239 Kcal.

The starch components, including total starch and resistant starch were determined with a Megazyme assay kit (Megazyme International Ireland, Bray Business Park, Bray, Ireland) as described by McCleary *et al*. (1994). Amylose : amylopectin ratio was also determined with the Megazyme amylase : amylopectin assay kit using the selective quantitative precipitation reaction of concanavalin A (ConA) with amylopectin (Gibson *et al.*, 1996).

The concentrations of amino acids were determined at the Australian Proteome Analysis facility at Macquarie University using pre-column derivatisation of amino acid analysis with 6- aminoquinoly-N-hydroxysuccinimidyl carbamate (AQC) followed by separation of the derivative and quantifications by reversed phase high performance liquid chromatography (HPLC). Minerals were analyzed by the inductively coupled plasma (ICP) method (Vista MPX-radial) as described by Anderson & Henderson (1986). The sealed chamber digest (SCD) method was used for quantification of P, S, K, Na, Mg and trace mineral elements. Non-starch polysaccharide (NSP) content was measured by gas chromatography (VARIAN, CP-3800, USA) according to the methods of Englyst & Hudson (1993) and Theander & Westerlund (1993).

The *in vitro* digestibility of dry matter (DM), starch and CP was determined by the method of Babinszky (1990) with slight modifications. Briefly: 12.5 mL of 0.1 N HCl containing 4 g/L pepsin (Sigma Chemical, St Louis, Mo, USA) was mixed with 500 mg of maize samples and then the mixture was gently shaken in a waterbath at 40 °C for 1.5 h. After neutralization with 110 mg $NaHCO_3$ (2 mL in each tube), the digesta was mixed with 12.5 mL of 0.2 M potassium phosphate buffer containing pancreatin (4 g/L) and amylase (4 mL/L), and incubated at 40 °C for 3 h with occasional vortexing to simulate the pancreatic phase of digestion. After incubation, 2.5 mL of $NaCO_3$ (100 g/L) was added to each tube and the content was centrifuged at 1643 g for 20 min. Afterwards, the supernatant was kept on ice until viscosity analysis, followed by repeated rinsing of the residue with MQ water. The residue was used for the calculation of DM and determination of glucose, which was converted to starch for estimation of starch digestibility. The DM and starch digestibility were calculated by the following equations.

DM digestibility (%) = (weight of maize sample – weight of dried residue)/weight of maize grain × 100

Starch digestibility (%) = (starch % of maize grain – starch % of dried residue)/starch % of maize grain × 100

In vitro viscosity of thawed supernatants was measured with a Brookfield DVIII viscometer at 25 °C with a CP40 spindle speed of 100 rpm. The grains were scanned on a NeoScope, JCM-5000, table-top SEM, (JEOL Ltd, Tokyo, Japan). Whole grains were scoured around the edges and cut in section, then mounted on the machine for assessment at a magnification of x1000.

The data were subjected to non-parametric analysis using SPSS (SPSS Statistics version 17.0.0, 2009) followed by calculation of coefficient of variation (CV).

Results

The proximate components of the different batches of maize are shown in Table 1. The mean DM and ash content of all grain batches varied between 870 and 980 g/kg, and 1.23 and 1.32 g/kg, respectively. The DM and ash content were higher in artificially dried grains than in the sun-dried grain. However, there was not much difference (3%) in DM and ash content between the three heat-treated groups. The CP, EE and phytate-P content varied between 93.8 and 98.4; 41.3 and 45.0 and 1.21 and 1.80 g/kg, respectively, in the samples dried at 80, 90 and 100 °C. These values were sharply decreased with increasing drying temperature.

The concentrations of key amino acids such as methionine, threonine, alanine, phenylanaline, arginine, leucine, isoleucine and valine were increased by artificial drying compared to sun-drying. In addition, the concentration tended to increase with an increase in drying temperature. Among the amino acids, lysine concentration was not increased by artificial drying. The methionine, lysine, leucine and isoleucine concentrations were the most variable amino acids among the groups.

Table 1 Composition of maize batches obtained by sun drying or artificially dried at different temperatures

A. Proximate components (g/kg DM), phytate-P (g/kg DM) and energy (MJ/kg DM)

	DM	CP	EE	Ash	Phytate-P	GE	ME
Sun drying	870.0	98.4	45.0	1.23	1.80	18.9	12.7
80 °C	950.0	93.4	42.0	1.29	1.36	18.4	13.6
90 °C	963.0	92.2	42.1	1.30	1.35	18.4	13.6
100 °C	980.0	93.8	41.3	1.32	1.21	18.5	14.0
CV	00.05	0.03	0.04	0.03	0.18	0.01	0.04
s.e.m.	24.34	1.36	1.73	0.03	0.05	0.11	0.27

B. Amino acids (g/kg DM)

	Met	Lys	Thr	Ala	Phe	Arg	Leu	Ile	Val
Sun drying	1.2	2.2	3.0	6.4	4.3	4.2	10.3	3.3	4.1
80 °C	1.4	2.0	3.1	6.8	4.4	4.3	11.2	3.7	4.3
90 °C	1.4	1.9	3.2	6.9	4.6	4.2	11.7	3.6	4.4
100 °C	1.3	1.9	3.3	7.0	4.7	4.3	11.9	3.8	4.4
CV	0.08	0.08	0.03	0.04	0.04	0.01	0.07	0.06	0.03
s.e.m.	0.05	0.08	0.05	0.13	0.09	0.03	0.37	0.11	0.07

C. Starch content and components (g/kg DM)

	Starch	Resistant starch	Amylopectin	Amylose	Amylose: Amylopectin
Sun drying	670	317	390	280.3	0.72
80 °C	691	363	388	303.7	0.78
90 °C	688	366	380	308.0	0.81
100 °C	684	416	370	313.8	0.85
CV	0.02	0.11	0.02	0.05	0.07
s.e.m.	4.65	20.3	42.5	7.35	0.10

D. Minerals

	Macro elements (g/kg DM)					Micro elements (mg/g DM)			
	Ca	P	Na	K	Mg	Mn	Zn	Fe	Cu	Mo
Sun drying	0.05	2.9	7.9	3.5	1.6	6.2	17.0	37.4	1.0	0.43
80 °C	0.05	2.6	7.3	3.3	1.4	8.7	15.4	27.9	1.1	0.43
90 °C	0.04	2.5	7.1	3.1	1.3	5.1	14.0	25.2	1.1	0.39
100 °C	0.03	2.6	7.0	3.2	1.4	5.6	14.9	18.7	1.5	0.39
CV	0.23	0.08	0.05	0.05	0.08	0.25	0.08	0.28	0.19	0.06
s.e.m.	0.00	0.11	0.19	0.09	0.05	0.80	0.63	3.88	0.11	0.01

DM - dry matter; CP - crude protein; EE - ether extract; phytate-P – phytate phosphorus (g/kg DM); GE - gross energy; ME - metabolisable energy (MJ/kg DM).

CV - Coefficient of variation; s.e.m. - Standard error of the mean.

The total starch content varied between 670 g/kg in the sun-dried samples and 691 g/kg in samples dried at 80 °C. Resistant starch and amylose content were also increased with an increase in heating temperature, being highest in samples dried at 100 °C (415 and 314 g/kg, respectively) than in the other groups. Compared to the sun-dried samples, the concentrations of starch, RS and amylose were increased by 2.1%, 31.3% and 12.0%, respectively for the grains dried at 100 °C. Conversely, the content of amylopectin was reduced between 16.3% (80 °C) and 27.2% (100 °C) when compared with the sun-dried samples. The GE content was decreased by 2.2% but ME content, estimated from nutrient composition, was increased by 9.3%. The content of resistant starch, amylopectin and the ratio of amylase : amylopectin were the most variable of the starch components, as shown by the CV.

There were lower concentrations of most micro elements in the artificially dried samples than in sundried maize. Drying of maize at 100 °C resulted in lower manganese, zinc and iron concentrations than drying at 90 °C and 80 °C. The concentrations of calcium, manganese, iron and copper were more variable in terms of CV than in the other minerals.

The total soluble NSP content varied from 3.29 to 3.79 g/kg, being generally higher in the artificially dried grains than in the sun-dried samples (Table 2). Ribose, arabinose, xylose and galactose were the most variable of the component sugars. There was very little variation (64.2 to 66.1 g/kg) in the concentrations of insoluble NSP, with the CV being generally lower than 0.05. In the case of available free sugar content, xylose and mannose were the most variable of the free sugar component.

Table 2 Non-starch polysaccharide (NSP) components of maize batches observed under varying drying temperatures

A. Soluble NSP content and components (g/kg DM)

	Rib	Ara	Xyl	Man	Gal	Glu	NSP
Sun drying	0.05	0.55	0.35	1.89	0.34	0.50	3.29
80 °C	0.08	0.77	0.46	1.84	0.43	0.60	3.87
90 °C	0.07	0.76	0.46	1.86	0.40	0.58	3.69
100 °C	0.08	0.85	0.49	1.83	0.39	0.61	3.79
CV	0.19	0.17	0.14	0.01	0.10	0.09	0.07
s.e.m.	0.01	0.06	0.03	0.01	0.02	0.03	0.13

B. Insoluble NSP content and components (g/kg DM)

	Ara	Xyl	Man	Gal	Glu	NSP
Sun drying	20.1	25.3	1.00	5.71	22.34	66.1
80 °C	19.4	24.7	0.94	5.29	21.98	64.21
90 °C	19.6	25.3	0.93	5.50	22.93	65.87
100 °C	19.4	25.3	0.93	5.38	22.60	65.33
CV	0.02	0.01	0.04	0.03	0.02	0.01
s.e.m.	0.16	0.16	0.02	0.09	0.20	0.42

C. Available free sugars content and components (g/kg DM)

	Ara	Xyl	Man	Gal	Glu	NSP
Sun drying	0.36	0.11	2.12	0.32	16.6	19.48
80 °C	0.34	0.10	1.75	0.31	15.65	18.06
90 °C	0.37	0.09	1.74	0.31	15.66	18.12
100 °C	0.39	0.11	1.76	0.29	15.05	17.55
CV	0.06	0.09	0.10	0.04	0.04	0.05
s.e.m.	0.01	0.005	0.09	0.01	0.31	0.41

CV - Coefficient of variation, s.e.m. - Standard error of the mean.

The mean *in vitro* DM and starch digestibility values of all the grain batches varied from 48.0 to 52.5 and 57.6 to 63.0, respectively (Table 3). The results indicated that digestibility of DM was improved by artificially drying the HM maize but starch digestibility was reduced. There was no effect of treatment on *in vitro* digesta viscosity.

Table 3 *In vitro* dry matter, starch and CP digestibility and viscosity of maize batches observed under varying drying temperatures

Treatment	Digestibility		Viscocity[1]
	Dry matter	Starch	
Sun drying	48.0	63.0	0.92
80 °C	52.4	58.2	0.91
90 °C	52.3	57.6	0.91
100 °C	52.5	58.4	0.90
CV	0.04	0.04	0.009
s.e.m.	1.10	1.24	0.004

[1] cp (in centipoises) - 1/100dyne second per centimetre^2; CV - coefficient of variation.

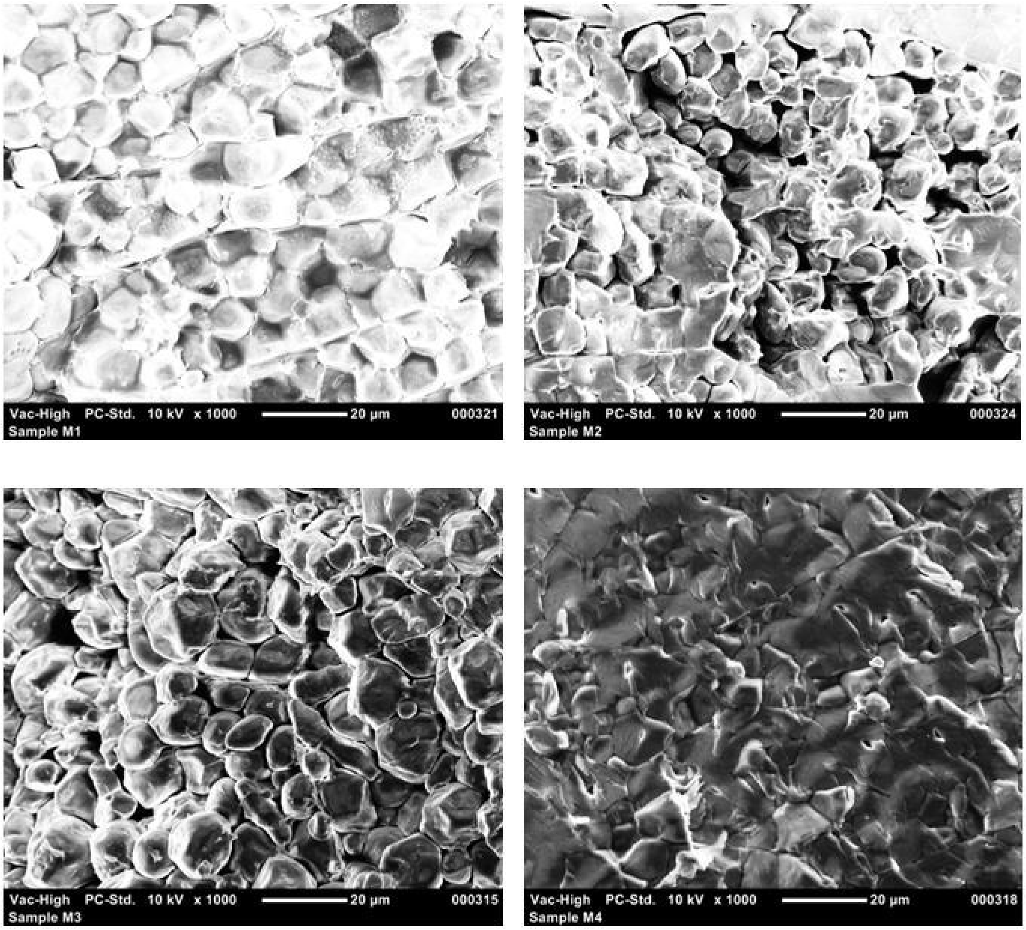

Plate 1 Electron microscope images (X1000) of fresh maize - sundried (top left) or dried at 80 °C (top right), 90 °C (bottom left) and 100 °C (bottom right).

The scanning electron micrographs of the different grains revealed variation in the morphology of the starch granules (Plate 1). The granules shrank in size as a result of artificial drying of the grains. The degree of shrinkage of granules was increased with increasing drying temperature. The internal matrix of the grains, which reflects the linkage of starch and protein bodies, was also different.

Discussion

In the present study, further drying of high moisture maize grains led to a considerable reduction in moisture content but variable changes in solid components. Drying at 100 °C tended to reduce the concentration of CP, EE and phytate-P. Similar findings were reported by Iji *et al.* (2003) who observed a reduction in the concentrations of ether extract and energy in maize grain due to drying grains at high temperatures.

The reduction in phytic acid content through drying may be useful as this chelate reduces the activity of pepsin, trypsin and α-amylase, which are very important for digestion of key nutrients (Sebastiana *et al.*, 1998). Artificial drying also resulted in an increase in the concentration of most essential amino acids. This may have some implication for feed formulation as grains tend to be classified with the same nutrient composition regardless of how they were dried.

Higher drying temperatures tended to increase the starch, resistant starch, amylose and amylase : amylopectin ratio of samples. Although, resistant starch is formed during seed formation, its proportion may increase during feed processing, especially drying (Brown, 1996) and storage. While most maize is sun-dried *in situ*, wet weather may necessitate the use of artificial drying techniques. Artificial drying results in the annealing of starch, while long periods of sun drying have been known to cause stack-burn, a defect in the quality of the crop.

Increases in amylose and its ratio with amylopectin, as well as in resistant starch signify a decline in quality of maize grains (Ito *et al.*, 1999). However, the results differ from those of Iji *et al.* (2003), but this may be due to differences in initial moisture content. The energy content also decreased with heating, probably due to the volatilization of fat. Some studies in poultry have shown that the apparent metabolizable energy (AME) values of cereal grains can vary considerably depending on time after harvest. There is a strong link between the EE and energy contents, lipids being considerably higher in energy than protein or carbohydrate.

The extent of starch chain associations within amorphous regions and the degree of crystalline order are altered during heat treatment of HM grains (Hoover & Vasanthan, 1994). The magnitudes of these changes, especially the varying proportions of amylose and amylopectin, were found to be dependent upon the moisture content during heat treatment and the starch sources.

In the present study, soluble NSP content was increased as a result of oven drying of maize grains. Soluble NSP are responsible for the reduction in productivity of diets based on temperate cereals but are generally low in maize and other tropical cereals (Choct & Annison, 1992). This may be responsible for the low viscosity of the *in vitro* digesta in this study.

Cereal grains are principally fed to provide energy, and processing techniques must be designed to maximize total digestibility of the diet as a primary objective. The *in vitro* starch digestion was decreased as a result of artificial drying of the grains, and this may be due to increased amylose content. These findings are supported by those of Panigrahi *et al.* (1996). The increase in the content of resistant starch suggests a loss in grain quality since resistant starch is not responsive to animal enzymes (Noy & Sklan, 1994). On the other hand, these findings disagree with those of Nir *et al.* (1993) who reported a 4.5 fold increase in *in vitro* digestion of maize starch by amylase after heat treatment.

Different types of starch granules were observed in the different batches. The starch granules of maize are large and essentially spherical in shape in the fresh grains (Taylor & Belton, 2002). In the present study most of the starch granules were squeezed, some of them overlapped each other and the granules were tightly packed in response to artificial drying. The size of the starch granule is an important factor in determining the energy value of grain, starch with smaller granules having a relatively larger surface area and so a greater potential for hydrolysis by endogenous amylase (Carre, 2004). During heat processing, the starch gelatinizes to an extent that is dependent on granule size, moisture content, amylase : amylopectin ratio and time (Klucinec & Thompson, 1999; Tester *et al.*, 2004).

Conclusions

From the present study it can be concluded that HM maize is affected by artificial drying and such treatment may change the chemical composition of the grains considerably. The changes in starch composition may significantly affect the nutritive value of the grains. These effects were most pronounced at 100 °C. If it is necessary for HM maize to be artificially dried then drying temperature should be lower than 100 °C. Further studies will be conducted into the feeding value of the grains when included in diets for chickens.

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