Effect of forced convection roasting on physicochemical and antioxidant properties of whole grain maize (*Zea mays* L.) and optimisation of roasting conditions

by

Shuaibu Mallam Bala

Dissertation presented for the degree of
Doctor of Philosophy (Food Science) in the Faculty of AgriSciences
at
Stellenbosch University

Supervisor: Prof. Marena Manley
Co-Supervisor: Prof. Umezuruike Linus Opara

March 2016

Declaration

By submitting this dissertation electronically, I declare that the entirety of the work contained therein is my own, original work, that I am the sole author thereof (save to the extent explicitly otherwise stated), that reproduction and publication thereof by Stellenbosch University will not infringe any third party rights and that I have not previously in its entirety or in part submitted it for obtaining any qualification.

Shuaibu Mallam Bala

March 2016

Acknowledgements

All praises and gratitude are due to Allah, The Almighty. May His peace and blessings be upon Prophet Muhammad (SAW).

It has really been a long and tedious journey. AhamdulilLah! I earnestly thank and appreciate the enormous contributions of the following people and organisations towards the success of my academic carrier in particular and life in general:

My parents, for taking good care of me from the cradle and continuous affection, prayers, encouragement and constructive advice; my siblings and relatives for support, motivation and encouragement;

A special thanks to my beloved wife (Ruqayyah) and daughter (Amirah) for their unconditional love, concern, perseverance, patience, good will, trust, advice and having full confidence in me; well appreciated indeed!

My supervisor, Prof. Marena Manley, for her excellent and highly professional supervision, hard work, patience, constructive advice, trustworthiness, motivation, encouragement, kindness and mentorship; Baie dankie!

My co-supervisor, Prof. Umezuruike Linus Opara, for his skilled guidance, advice and mentorship, motivation, fatherly encouragement, kindness, support and patience.

West Africa Agricultural Productivity Programme (WAAPP-Nigeria), for full financial sponsorship of the PhD programme;

Ahmadu Bello University, Zaria-Nigeria, my employer, for granting me the fellowship to further my education;

South African Research Chairs Initiative of the Department of Science and Technology and National Research Foundation for the use of their well-equipped laboratory and conducive study office;

Agricol (Seed Company), Brackenfell for the providing force convection continuous tumble roaster and the use of facilities; a special appreciation to Mr. Johan du Plooy for his assistance with installation and use of the roaster;

I also appreciate the contributions of Prof. Martin Kidd in experimental design, statistical data analyses and interpretation, Dr. O.A Fawole in antioxidant determinations, statistical data analyses and interpretation and Dr. C.J Oluwafemi for advice and encouragement.

This dissertation is presented in the format of the Department of Food Science at Stellenbosch University. The structure is in the form of one or more research chapters (papers prepared for publication) and is prefaced by an introduction chapter with the study objectives, followed by a literature review chapter and culminating with a chapter for elaborating a general discussion. Language, style and referencing format used are in accordance with the requirements of the International Journal of Food Science and Technology. This dissertation represents a compilation of manuscripts where each chapter is an individual entity and some repetition between chapters has, therefore, been unavoidable.

Dedication

This dissertation is wholeheartedly dedicated to Allah (SWT), the Creator of the universe.

…… and say: My Lord increase me in knowledge.

Holy Qur'an 20:114

Abstract

Maize (*Zea mays* L.) is the most cultivated cereal and grain crop in the world and it is used as a staple food in developing countries such as Nigeria, South Africa, Mexico and economically less privileged countries. The grains of maize are processed into intermediate products (flour and meal) which are utilised for the production of different types of ready to eat foods. In most cases, the flour or meal used is refined (bran and germ removed) and not pregelatinised. Heat-processing methods of maize that uses dry heat reduced the nutritional quality of intermediate and end products. Forced convection roasting (FCR), a novel heat-processing technique, that has an additional advantage of using superheated steam was used to study the changes in physicochemical, proximate composition and antioxidant properties of Nigerian (S28, S33) and South African (H2G1, H7D1) maize varieties. Roasting temperature and rotating speed (determining roasting time) limits (150 to 220 °C) and (30 to 90 Hz), respectively were used for the roasting in a forced convection continuous tumble roaster (FCCTR). Roasting conditions (temperature/rotating speed) of the maize varieties were optimised for the production of whole grain flour or meal. Comparison of the proximate composition, antioxidant and pasting properties of the optimally processed whole grain flour or meal with raw whole grain flour or meal and an unroasted refined commercial maize meal (CMM) was made.

The nutritional quality and antioxidant properties (content and activity) of the Nigerian maize S28 (yellow kernel) and S33 (white kernel) were not negatively affected by FCR. For the South African maize varieties, FCR did not show a negative effect on the proximate composition and antioxidant properties except the increase in total phenolics content of H2G1. Variations in the physicochemical properties such as bulk density, kernel hardness, colour and pH of the roasted maize varieties did not compromise the quality of the optimally processed whole grain flours. The prediction models of moisture content, whiteness index (WI), yellowness index (YI), total essential amino acids (TEAA) and total amino acids (TAA) had good fit (R^2 >0.8) with the experimental data and non-significant (p ≤0.05) lack-of-fits. The desirability profiling of moisture content, WI and YI indicated 189.9 °C/90 Hz and 140.9 °C/49.8 Hz as the mean optimum roasting conditions of S28 and S33 maize varieties, respectively for the production of high quality whole grain flour or meal. Similarly, the desirability profiling of moisture content, WI, YI, TEAA and TAA showed the mean optimum roasting conditions of H2G1 and H7D1 white maize varieties to be 185.0 °C/65.5 Hz and 182.6 °C/55.0 Hz, respectively.

The carbohydrate, crude protein, fat and fiber, ash, total phenolics and flavonoids as well as free radical scavenging capacity of the optimally processed whole grain flours did not significantly differ from those of the raw whole grain flours of each of the maize varieties. Both whole grain flours of the raw and roasted maize grains had higher proximate composition, total phenolics, total flavonoids and antioxidant activity than CMM, except the carbohydrate content which was found to significantly higher in the later. The optimally processed whole grain flour of each maize variety

had a non-significantly lower pasting temperatures and significantly higher pasting viscosities compared to the raw whole grain flour. This indicated better pasting characteristics of the optimally processed whole grain flours with reference to the raw whole grain flours of the maize varieties. However, CMM had significantly lower pasting temperatures and higher pasting viscosities than the whole grain flours which indicated better pasting properties of the former.

Considering the non-negative effect on proximate composition and antioxidant properties, and better pasting characteristics of whole grain flours of the roasted maize varieties, it could be concluded that FCR is a good alternative for roasting maize grains in the process of producing whole grain flours with the best quality for human consumption. It was also observed that the whole grain flours had better nutritional and antioxidant properties, but poorer pasting properties compared to CMM.

Uittreksel

Mielies (*Zea mays* L.) is die mees gekweekte graan in die wêreld en word gebruik as 'n stapelvoedsel in ontwikkelende lande soos Nigerië, Suid-Afrika, Mexiko en ekonomies minder bevoorregte lande. Mieliepitte word geprosesseer vir die produksie van intermediêre produkte (meel en mieliemeel) vir die vervaardiging van verskillende tipes gereed-om-te-eet kosse. In die meeste gevalle is die meel of mieliemeel wat gebruik word, verfyn (semel en kiem is verwyder) en ook nie voorheen gegelatiniseer nie. Hitte-verwerkingsmetodes wat van droë hitte gebruik maak, verlaag die voedingswaarde van die mielie se intermediêre en finale produkte. Geforseerde-konveksie-verroostering (GKV), 'n nuwe hitte-prosesseringstegniek met 'n ekstra voordeel omdat dit gebruik maak van super-verhitte stoom, is gebruik om die veranderinge in die fisiochemiese eienskappe, voedingswaarde en antioksidant eienskappe van Nigeriese (S28, S33) en Suid-Afrikaanse (H2G1, H7D1) mieliebasters te bestudeer. Die volgende limiete is gebruik vir die verroostering: verroosteringstemperature (150 tot 220 °C) en verroosteringsspoed (30 to 90 Hz) soos gebruik gemaak tydens die geforseerde-konveksie-aaneenlopende-tuimelende-verroosteringsproses (GKATV). Verroostereingstoestande (verroosteringstemperature / rotasiespoed) van die mieliebasters is geoptimaliseer vir die produksie van heelgraan, sowel as meel of mieliemeel. Die voedingwaarde, antioksidant- en vergellingseienskappe van die geoptimaliseerde produksie van die heelgraanmeel of mieliemeel, saam met ongeroosterde heelgraanmeel of mieliemeel en 'n verfynde kommersiële mieliemeel (KMM), is met mekaar vergelyk.

Die voedingswaarde en antioksidanteienskappe (inhoud en aktiwiteit) van die Nigeriese mieliebasters S28 (geel mielie) en S33 (wit mielie) is nie negatief geaffekteer deur GKV nie. Die Suid-Afrikaanse mieliebasters wat blootgestel is aan GKV, het nie enige negatiewe effekte met betrekking tot die voedingswaarde en antioksidanteienskappe getoon nie, behalwe die toename in totale polifenolinhoud van H2G1. Variasie in die fisiochemise eienskappe soos bulk-digtheid, pit hardheid, kleur en pH van die geroosterde mieliebasters het nie die kwaliteit van die optimaal-geprosesseerde heelgraanmele beïnvloed nie. Die voorspellingsmodelle van die voginhoud, witheidsindeks (WI), geelheidsindeks (GI), totale essensiële aminosure (TEA) en totale aminosure (TA) het goeie verband getoon (R^2 >0.8) met die eksperimentele data wat nie-beduidende (p ≤0.05) gepas het. Die gewenste profiel van die voginhoud, WI en GI het daarop gedui dat 189.9 °C/90 Hz en 140.9 °C/49.8 Hz die gemiddelde optimale verroosteringskondisies vir S28 en S33 mieliebasters, onderskeidelik, was vir die produksie van hoë kwaliteit heelgraanmeel of mieliemeel. Soortgelyk het die gewenste profiel vir die voginhoud, WI, GI, TEA en TA daarop gewys dat die gemiddelde optimale verroosteringskondisies vir H2G1 en H7DI witmieliebasters onderskeidelik 185.0 °C/65.5 Hz en 182.6 °C/55.0 Hz was.

Die koolhidraat-, ru-protein-, vet en vessel-, as-, totale fenole- en flavanoïde inhoud, asook die vry-radikaal-aas-kapasiteit van die optimaal-geprosesseerde heelgraanmele het nie-beduidend

van die rou heelgraanmele verskil, vir elk van die mieliebasters. Beide heelgraanmele van die rou en geroosterde mielies het 'n hoër ru-protein-, vet en vesel, as-, totale fenole- en flavanoïde inhoud, asook vry-radikaal-aas-kapasiteit getoon as die KMM, behalwe die koolhidraat inhoud wat beduidend hoër was in die KMM. Die optimaal-geprosesseerde heelgraanmele van elk van die mieliebasters het 'n nie-beduidend laer vergellingstemperatuur en 'n hoër vergellingsviskositeit getoon in vergelyking met die rou heelgraanmeel. Dit het gedui op beter vergellingseienskappe vir die optimaal-geprosesseerde heelgraanmele met verwysing na die rou heelgraanmele van die mieliebasters. Nieteenstaande het die KMM beduidend laer vergellingstemperature en hoër vergellingsviskositeit getoon as dié van die heelgraanmele wat daarop gedui het dat die vergellingseienskappe van laasgenoemde beter was.

As die koolhidraat-, ru-protein-, vet en vessel-, as-, totale fenole- en flavanoïde inhoud en die vry-radikaal-aas-kapasiteit, asook die vergellingseienskappe van die heelgraanmele van die mieliebasters in ag geneem word, kan daar tot die gevolgtrekking gekom word dat GKV 'n beter alternatief vir verroostering van mielies is vir die produksie van heelgraanmele om die beste kwaleiteit vir menslike gebruik. Dit is ook opgemerk dat die heelgraanmele beter voedingswaarde en antioksidant eienskappe gehad het, alhoewel swakker vergellingseienskappe in vergelyking met KMM.

List of conference papers presented

1. **Shuaibu Mallam Bala**, Marena Manley and Umezuruike Linus Opara (2014). Effect of forced convection roasting on moisture loss, bulk density and colour of two South African maize (*Zea mays* L.) varieties. Presented (oral) at the *1ˢᵗ New Voices in Cereal Sciences and Technology Symposium,* **Pretoria, South Africa**. September 3 – 4, 2014.

2. **Shuaibu Mallam Bala,** Umezuruike Linus Opara, Martin Kidd and Marena Manley (2014). Effect of forced convection roasting on the physicochemical and antioxidant properties of Nigerian maize (*Zea mays* L.). Presented (poster) at the *21ˢᵗ South African Association of Food Science and Technology (SAAFoST) International Congress and Exhibition,* **Durban, South Africa**. September 7 – 9, 2015.

3. **Shuaibu Mallam Bala,** Umezuruike Linus Opara, Martin Kidd and Marena Manley (2014). Optimisation and effect of forced convection roasting on physicochemical and antioxidant properties of Nigerian maize cultivars. Presented (poster) at the *International Centennial (100ᵗʰ) Meeting of the American Association of Cereal Chemists International (AACCI),* **Minneapolis, USA**. October 18 – 21, 2015.

4. **Shuaibu Mallam Bala,** Umezuruike Linus Opara, Martin Kidd and Marena Manley (2014). Effect of forced convection roasting on physicochemical and antioxidant properties and optimisation of roasting conditions of South African maize (*Zea mays* L.) hybrids for the production of whole grain meal. Presented (poster) at the *29ᵗʰ European Federation of Food Science and Technology (EFFoST) International Conference,* **Athens, Greece***. November 10 – 12, 2015***.** Published in book of proceedings of the conference, Volume II, Pp 806 – 811.

Table of Contents

List of Figures

List of Tables

List of abbreviations used

A:	Absorbance
a*:	Redness
AACCI:	American Association of Cereal Chemists International
AAE:	Ascorbic acid equivalent
ABTS:	2,2′-Azino-bis(3-ethylbenzoline-6-sulfonic acid) diammonium salt
A_c:	Absorbance of control
AD:	After death
A_E:	Absorbance of reaction mixture containing extract
ANOVA:	Analysis of variance
APC:	Adjusted protein content
β:	Regression coefficient
b*:	Yellowness
BV:	Breakdown viscosity
AOAC:	Association of Official Analytical Chemists
BD:	Bulk density
C:	Center point
CAF:	Central analytical facility
CCD:	Central composite design
CE:	Catechin equivalent
C/F:	Coase to fine ratio
CIMMYT:	International maize and wheat improvement center
CMM:	Commercial maize meal
cP:	Centipoise
CPT:	Cereal process technologies
D:	Overall desirability function
d_i:	Individual desirability function
3D:	Three dimensional
DM:	Dry matter

DNA:	Deoxyribonucleic acid
DPPH:	2,2-Diphenyl-1-picrylhydrazyl
Eq:	Equation
ESI:	Electrospray ionisation
FCCRT:	Forced convection continues tumble roaster
FCR:	Forced convection roasting
FDA:	Food and drug administration
FMC:	Final moisture content
FV:	Final viscosity
GAE:	Gallic acid equivalent
kV:	Kilo volt
IL:	Interaction linear effect
L:	Linear
*L**	Lightness
LC:	Liquid chromatography
LSD:	List significant difference
M:	Molarity
MMT:	Million metric ton
MS:	Mass spectrometry
N:	Normality
NAS:	National Academy of science
NCM:	National chamber of milling
OMC:	Original moisture content
PC:	Principal component
PCA:	Principal component analysis
PSI:	Particle size index
PT:	Pasting temperature
PV:	Pasting viscosity
Q:	Quadratic

QPM:	Quality protein maize
r:	Roasted
R^2:	Coefficient of determination
RSM:	Response surface methodology
RVA:	Rapid viscos analyser
S.E:	Standard error
SL:	Speed linear effect
SPC:	Soy protein concentrate
SQ:	Speed quadratic effect
SV:	Setback viscosity
TAA:	Total amino acids
TEAA:	Total essential amino acids
TF:	Total flavonoids
TL:	Temperature linear effect
TP:	Total phenolics
TQ:	Temperature quadratic effect
TV:	Trough viscosity
UPLC:	Ultra-performance liquid chromatography
Ur:	Unroasted
USA:	United States of America
USDA:	United State Department of Agriculture
UV:	Ultraviolet
V:	Volt
WAC:	Water absorption capacity
WI:	Whiteness index
WSI:	Water solubility index
YI:	Yellowness index
Y:	Response variable

CHAPTER ONE

Chapter 1

General Introduction

Maize (*Zea mays* L.), a cereal crop, also known as corn in many English-speaking countries was domesticated in prehistoric times by the indigenous people of Mesoamerica (Ensminger & Ensminger, 1993; Piperno & Flannery, 2001). The scientific classification of maize is as follows: Kingdom: Plantae, Order: Poales, Family: Poaceae, Subfamily: Panicoideae, Tribe: Andropogoneae, Genus: Zea, Species: *mays*. The leafy stalk of the maize plant (Fig. 1.1) produces maize ears, which contain seeds called kernels. Technically, maize kernels are considered as maize grains (Fig. 1.1). The Olmec and Meyans cultivated maize of different varieties throughout central and southern Mexico (Wilkes, 2004). Between 1700 and 1250 AD, maize spread through much of the Americas (North, Central and South America). The region developed a trade network based on surplus and varieties of maize grains produced. After contact by Europeans with the Americas in the late 15th and early 16th centuries, explorers and traders carried maize grains back to Europe and introduced them to other countries (Roney & Hard, 2009). Maize was spread to the rest of the world due to its ability to grow in diverse climatic conditions. The colour of maize kernels are predominantly white and yellow, and depending on the variety some could be blackish, purple, bluish-grey, green or red.

Figure 1.1. Maize (a) plant and (b) kernels.

In terms of production, maize is the most cultivated cereal and grain crop in the world. The United States Department of Agriculture (USDA) reported about 990 million metric tons (MMT) as the total global production of maize in 2014 with the United States of America (USA) being the largest producer (366 MMT) (USDA, 2015). South Africa and Nigeria were the 8th and 13th world largest maize

2

producers in 2014 with total production of 13.5 and 7.5 MMT, respectively. In developed countries such as the USA, maize is used as raw material in pharmaceutical, food and confectionery industries, and production of animal feed with about 40% used for the production of bio-ethanol (Pollack, 2011). However, in developing countries such as Nigeria and South Africa, most of the maize produced is consumed as staple food by human beings. For human consumption, maize is processed by boiling, baking, extrusion, nixtamalisation and roasting (Bolade *et al.*, 2009). One of the most popular products of maize consumed in Nigeria and other West African countries is known as *Tuwo* which is a gel-like product made with non-fermented maize flour and hot water (Bolade, 2010). It is usually served with different types of vegetable soup and meat or fish. The production and consumption of *Tuwo* is similar to that of *Mielie pap* (porridge) in South Africa and other Southern African countries. The only difference is that *pap* is made with coarser maize flour (maize meal).

The maize flour and meal used in Nigeria and South Africa, respectively, are not pregelatinised. Gelatinisation is the irreversible structural changes of starch granules due to rise in temperature and increase in moisture (Waigh *et al.,* 2000) resulting in amylose leaching and increased digestibility. Production of maize flour and meal involves the removal of the bran and germ. The bran contains dietary fiber, minerals, vitamins and phytochemicals, while the germ is rich in protein, unsaturated fat, minerals and vitamins of nutritional importance. Whole grain consumption provides diets of superior quality and required nutrients (O'Neil *et al.*, 2010) for healthy growth and development. Phytochemicals in whole grains reduce or prevent certain diseases by acting as antioxidants against free radicals and reactive oxygen species (Kennedy & Knill, 2003). Consumption of foods made completely or in combination with whole grain was reported to significantly reduce and manage cardiovascular diseases (Jensen *et al.*, 2004), cancer (Schatzkin *et al.*, 2007), obesity (Good *et al.*, 2008), type 2 diabetes mellitus (de Munter *et al.*, 2007) and hypertension (Steffen *et al.*, 2003).

Various types of heat-processing methods are employed depending on the ingredients, environment, traditions and economy of people across the world. Heat-processing methods have been used for the production of different types of preprocessed ingredients. The ingredients include maize tortilla dough (nixtamal) produced by nixtamalisation for making tortilla chips, masa and bread (Kayacier & Singh, 2003; Aguayo-Rojas *et al.*, 2012; López-Martínez *et al.*, 2012; Adolphson *et al.*, 2013), instant flour from quality protein maize (QPM) and maize-lentil extrudates by extrusion (Reyes-Moreno *et al.*, 2003; Lazou & Krokida, 2010). Roasted maize grain was also used for the production of beverage and maize-bambara groundnut complementary foods (Uvere *et al.*, 2010; Chung *et al.*, 2011). Roasting of linseeds, peanuts, soybeans and maize grains caused gelatinisation of starch, increased flavours, enhanced antioxidant content and activity, and improved food quality and safety of intermediate and end products (Cämmerer & Kroh, 2009; Lee & Lee, 2009; Chung *et al.*, 2011). Furthermore, roasting was reported to increase the antioxidant activity of hazelnuts (*Corylus avellena*

L.) (Locatelli *et al.*, 2010), apricot (*Prunus armeniaca* L.) kernels (Durmaz & Alpaslan, 2007), small black soybeans (*Glycine max* L. Merrill) (Kim *et al.*, 2011), protected that of coffee beans [*Coffea canephora* (robusta)] (Nebesny & Budryn, 2003) and enhanced the aroma of pumpkin (*Cucurbita pepo* L.) seed oil (Siegmund & Murkovic, 2004). However, nixtamalisation caused loss of dietary fiber, phytochemicals and vitamins (Palencia *et al.*, 2003; Pappa *et al.*, 2010). Extrusion resulted in loss of heat-labile vitamins and reduction of amino acids through non-enzymatic browning caused by Maillard reaction (Ilo & Berghofer, 2003). Dry hot air (dry heat) roasting of hazelnuts above 120 ⁰C led to loss of thiamin (more than 50%) and a decrease in riboflavin and amino acids (Özdemir *et al.*, 2001). Electric hot plate roasting of maize varieties decreased crude protein, dietary fiber, phenolics and flavonoids content (Oboh *et al.*, 2010). Use of a heat-processing method that will mitigate these negative effects would be of great benefit to food producers and consumers.

A novel grain heat-processing method called forced convection roasting (FCR) has been developed with the additional option of using superheated steam instead of dry heat (Fritz, 2013). Superheated steam could be defined as the steam generated at a temperature higher than that of its boiling (evaporation) point. It is also known as dry steam and was used in impingement drying to improve the texture of food products (Moreira, 2001). During superheated drying of food products, the water removed in the process becomes part of the drying medium (hot air). Superheated steam was reported to be cleaner, cause less oxidation in foods and provide higher evaporation rate thereby mitigating the loss of nutritional values compared to dry heat during drying process (Moreira, 2001). The superheated steam is forced through the grains while continuously being mixed and moving through the roasting chamber of a forced convection continuous tumble roaster (FCCTR) (Fig. 1.2). Continuous tumbling of the roasting chamber and the superheated steam result in faster and even transfer of heat into the grains leading to uniform roasting. There are different models (based on roasting capacity, size, range of roasting temperature and speed) of the FCCTR and some grains, such as certain legumes (pea nuts) with high oil and protein content, do not require superheated steam in the process of roasting. Increase in *in vitro* protein digestibility, water absorption capacity, reduction in protein solubility and emulsifying capacity of marama beans [*Tylosema esculentum* (Burch) A. Schreib] dry roasted using FCCTR were communicated (Maruatona *et al.*, 2010). Acceptability of a composite porridge of sorghum (*Sorghum bicolor* L.) and the roasted marama bean flour was investigated and found to be preferred by consumers (Kayitesi *et al.*, 2010; Kayitesi *et al.*, 2012). Dry heating (roasting) of marama beans using FCCTR for more than 20 min at 150 ⁰C caused bitterness which was attributed to some phenolics (gallic and protocatechuic acids), saponins and other unidentified compounds (Nyembwe *et al.*, 2015). Forced convection oven was used for moist (steam injection) and dry roasting of hazelnuts in comparison to conventional hot air drum roasting (Alamprese *et al.*, 2009). Their result revealed that the storage period of hazelnuts roasted under

moist condition was longer due to delay in lipid peroxidation, high content of tocopherols and preservation of celluar integrity. To date no work has been published on forced convection roasting of maize or any other cereal grain using FCCTR and superheated steam.

Response surface methodology (RSM), a statistical technique for studying complex processes, has been successfully utilised in various food processing optimisation using central composite design (CCD) (Mendes *et al.*, 2001; Reyes-Moreno *et al.*, 2003; Milán-Carrillo *et al.*, 2004; Kahyaoglu, 2008; Uysal *et al.*, 2009; Youn & Chung, 2012). It can also be used for studying the effect of, and relationship between, experimental factors (input/process/independent variables) and response (output/dependent) variables. Additionally, RSM could be utilised in empirical building of models using a second-degree polynomial equation for the optimisation of process and/or response variables.

Figure 1.2. Forced convection continuous tumble roaster (FCCTR), model R100E.

1.1. Aim

The aim of this research was to investigate the effect of forced convection roasting on physicochemical and antioxidant properties of whole grain maize varieties from Nigeria and South

5

Africa and to optimise the roasting conditions using response surface methodology for the production of whole grain maize flour or meal.

1.2. Specific Objectives

i. To determine the effect of roasting temperature and rotating speed on the physicochemical and antioxidant properties of whole grain maize.

ii. To optimise the roasting conditions (roasting temperature and speed) of the maize varieties for the production of whole grain flour or meal with the best nutritional quality.

iii. To assess the changes in proximate composition, antioxidant and pasting properties of whole grain maize flours produced using the optimised roasting conditions and to compare the results with those of raw whole grain and refined commercial maize meal (CMM) flours.

1.3. References

Adolphson, S.J., Dunn, M.L., Jefferies, L.K. & Steele, F.M. (2013). Isolation and characterization of the microflora of nixtamalized corn masa. *International Journal of Food Microbiology,* **165,** 209-213.

Aguayo-Rojas, J., Mora-Rochín, S., Cuevas-Rodríguez, E., Serna-Saldivar, S., Gutierrez-Uribe, J., Reyes-Moreno, C. & Milán-Carrillo, J. (2012). Phytochemicals and antioxidant capacity of tortillas obtained after lime-cooking extrusion process of whole pigmented mexican maize. *Plant Foods for Human Nutrition,* **67,** 178-185.

Alamprese, C., Ratti, S. & Rossi, M. (2009). Effects of roasting conditions on hazelnut characteristics in a two-step process. *Journal of Food Engineering,* **95,** 272-279.

Bolade, M.K. (2010). Evaluation of suitability of commercially available maize grains for 'tuwo' production in nigeria. *African Journal of Food Science,* **4,** 371-381.

Bolade, M.K., Adeyemi, I.A. & Ogunsua, A.O. (2009). Influence of particle size fractions on the physicochemical properties of maize flour and textural characteristics of a maize-based nonfermented food gel. *International Journal of Food Science and Technology,* **44,** 646-655.

Cämmerer, B. & Kroh, L.W. (2009). Shelf life of linseeds and peanuts in relation to roasting. *LWT - Food Science and Technology,* **42,** 545-549.

Chung, H.-S., Chung, S.-K. & Youn, K.-S. (2011). Effects of roasting temperature and time on bulk density, soluble solids, browning index and phenolic compounds of corn kernels. *Journal of Food Processing and Preservation,* **35,** 832-839.

De Munter, J.S., Hu, F.B., Spiegelman, D., Franz, M. & Van Dam, R.M. (2007). Whole grain, bran, and germ intake and risk of type 2 diabetes: A prospective cohort study and systematic review. *PLoS Medicine,* **4,** 185-195.

Durmaz, G. & Alpaslan, M. (2007). Antioxidant properties of roasted apricot (*Prunus armeniaca* L.) kernel. *Food Chemistry,* **100,** 1177-1181.

Ensminger, M.E. & Ensminger, A.H. (1993). Foods & nutrition encyclopedia, two volume set (2nd Ed)*.* CRC Press.

Fritz, T. (2013). Backgound and working principle (operation manual) of forced convection continuous tumble roaster (FCCTR). Bloemfontein, South Africa: Roastech.

Good, C.K., Holschuh, N., Albertson, A.M. & Eldridge, A.L. (2008). Whole grain consumption and body mass index in adult women: An analysis of NHANES 1999-2000 and the USDA pyramid servings database. *Journal of the American College of Nutrition,* **27,** 80-87.

Ilo, S. & Berghofer, E. (2003). Kinetics of lysine and other amino acids loss during extrusion cooking of maize grits. *Journal of Food Science,* **68,** 496-502.

Jensen, M.K., Koh-Banerjee, P., Hu, F.B., Franz, M., Sampson, L., Grønbæk, M. & Rimm, E.B. (2004). Intakes of whole grains, bran, and germ and the risk of coronary heart disease in men. *The American Journal of Clinical Nutrition,* **80,** 1492-1499.

Kahyaoglu, T. (2008). Optimization of the pistachio nut roasting process using response surface methodology and gene expression programming. *LWT - Food Science and Technology,* **41,** 26-33.

Kayacier, A. & Singh, R.K. (2003). Textural properties of baked tortilla chips. *LWT - Food Science and Technology,* **36,** 463-466.

Kayitesi, E., De Kock, H.L., Minnaar, A. & Duodu, K.G. (2012). Nutritional quality and antioxidant activity of marama–sorghum composite flours and porridges. *Food Chemistry,* **131,** 837-842.

Kayitesi, E., Duodu, K.G., Minnaar, A. & De Kock, H.L. (2010). Sensory quality of marama/sorghum composite porridges. *Journal of the Science of Food and Agriculture,* **90,** 2124-2132.

Kennedy, J.F. & Knill, C.J. (2003). Food colloids: Fundamentals of formulation: E. Dickinson, R. Miller (Eds.); the royal society of chemistry, cambridge. *Carbohydrate Polymers,* **51,** 361-364.

Kim, H.G., Kim, G.W., Oh, H., Yoo, S.Y., Kim, Y.O. & Oh, M.S. (2011). Influence of roasting on the antioxidant activity of small black soybean (*Glycine max* L. Merrill). *LWT - Food Science and Technology,* **44,** 992-998.

Lazou, A. & Krokida, M. (2010). Functional properties of corn and corn–lentil extrudates. *Food Research International,* **43,** 609-616.

Lee, S. & Lee, J. (2009). Effects of oven-drying, roasting, and explosive puffing process on isoflavone distributions in soybeans. *Food Chemistry,* **112,** 316-320.

Locatelli, M., Travaglia, F., Coïsson, J.D., Martelli, A., Stévigny, C. & Arlorio, M. (2010). Total antioxidant activity of hazelnut skin (*Nocciola piemonte* PGI): Impact of different roasting conditions. *Food Chemistry,* **119,** 1647-1655.

López-Martínez, L.X., Parkin, K.L. & Garcia, H.S. (2012). Effect of processing of corn for production of masa, tortillas and tortilla chips on the scavenging capacity of reactive nitrogen species. *International Journal of Food Science and Technology,* **47,** 1321-1327.

Maruatona, G.N., Duodu, K.G. & Minnaar, A. (2010). Physicochemical, nutritional and functional properties of marama bean flour. *Food Chemistry,* **121,** 400-405.

Mendes, L.C., De Menezes, H.C., Aparecida, M. & Da Silva, A. (2001). Optimization of the roasting of robusta coffee (*C. canephora* Conillon) using acceptability tests and RSM. *Food Quality and Preference,* **12,** 153-162.

Milán-Carrillo, J., Gutiérrez-Dorado, R., Cuevas-Rodríguez, E., Garzón-Tiznado, J. & Reyes-Moreno, C. (2004). Nixtamalized flour from quality protein maize (*Zea mays* L.). Optimization of alkaline processing. *Plant Foods for Human Nutrition,* **59,** 35-44.

Moreira, R. G. (2001). Impingement drying of foods using hot air and superheated steam. *Journal of Food Engineering,* **49,** 291-295.

Nebesny, E. & Budryn, G. (2003). Antioxidative activity of green and roasted coffee beans as influenced by convection and microwave roasting methods and content of certain compounds. *European Food Research and Technology,* **217,** 157-163.

Nyembwe, P., Minnaar, A., Duodu, K.G. & De Kock, H.L. (2015). Sensory and physicochemical analyses of roasted marama beans [*Tylosema esculentum* (Burchell) A. Schreiber] with specific focus on compounds that may contribute to bitterness. *Food Chemistry,* **178,** 45-51.

O'neil, C.E., Nicklas, T.A., Zanovec, M. & Cho, S. (2010). Whole-grain consumption is associated with diet quality and nutrient intake in adults: The national health and nutrition examination survey, 1999-2004. *Journal of the American Dietetic Association,* **110,** 1461-1468.

Oboh, G., Ademiluyi, A.O. & Akindahunsi, A.A. (2010). The effect of roasting on the nutritional and antioxidant properties of yellow and white maize varieties. *International Journal of Food Science and Technology,* **45,** 1236-1242.

Özdemir, M., Açkurt, F., Yildiz, M., Biringen, G., Gürcan, T. & Löker, M. (2001). Effect of roasting on some nutrients of hazelnuts (*Corylus avellena* L.). *Food Chemistry,* **73,** 185-190.

Palencia, E., Torres, O., Hagler, W., Meredith, F.I., Williams, L.D. & Riley, R.T. (2003). Total fumonisins are reduced in tortillas using the traditional nixtamalization method of mayan communities. *The Journal of Nutrition,* **133,** 3200-3203.

Pappa, M.R., De Palomo, P.P. & Bressani, R. (2010). Effect of lime and wood ash on the nixtamalization of maize and tortilla chemical and nutritional characteristics. *Plant Foods for Human Nutrition,* **65,** 130-135.

Piperno, D.R. & Flannery, K.V. (2001). The earliest archaeological maize (*Zea mays* L.) from highland mexico: New accelerator mass spectrometry dates and their implications. *Proceedings of the National Academy of Sciences,* **98,** 2101-2103.

Pollack, A. (2011). US approves corn modified for ethanol. *The New York Times, February 2011.*

Reyes-Moreno, C., Milán-Carrillo, J., Gutiérrez-Dorado, R., Paredes-López, O., Cuevas-Rodrıguez, E. & Garzón-Tiznado, J. (2003). Instant flour from quality protein maize (*Zea mays* L). Optimization of extrusion process. *LWT-Food Science and Technology,* **36,** 685-695.

Roney, J. & Hard, R. (2009). The beginnings of maize agriculture. *Archaeology Southwest,* **23,** 4-12.

Schatzkin, A., Mouw, T., Park, Y., Subar, A.F., Kipnis, V., Hollenbeck, A., Leitzmann, M.F. & Thompson, F.E. (2007). Dietary fiber and whole-grain consumption in relation to colorectal cancer in the nih-aarp diet and health study. *The American Journal of Clinical Nutrition,* **85,** 1353-1360.

Siegmund, B. & Murkovic, M. (2004). Changes in chemical composition of pumpkin seeds during the roasting process for production of pumpkin seed oil (part 2: Volatile compounds). *Food Chemistry,* **84,** 367-374.

Steffen, L.M., Jacobs, D.R., Stevens, J., Shahar, E., Carithers, T. & Folsom, A.R. (2003). Associations of whole-grain, refined-grain, and fruit and vegetable consumption with risks of all-cause mortality and incident coronary artery disease and ischemic stroke: The atherosclerosis risk in communities (ARIC) study. *The American Journal of Clinical Nutrition,* **78,** 383-390.

USDA (2015). Corn production by country in 1000MT. United States Department of Agriculture. URL: www.indexmundi.com/agriculture/?commodity=corn Accessed 21/February/2015.

Uvere, P.O., Onyekwere, E.U. & Ngoddy, P.O. (2010). Production of maize-bambara groundnut complementary foods fortified pre-fermentation with processed foods rich in calcium, iron, zinc and provitamin a. *Journal of the Science of Food and Agriculture,* **90,** 566-573.

Uysal, N., Sumnu, G. & Sahin, S. (2009). Optimization of microwave–infrared roasting of hazelnut. *Journal of Food Engineering,* **90,** 255-261.

Waigh, T.A., Gidley, M.J., Komanshek, B.U. & Donald, A.M. (2000). The phase transformations in starch during gelatinisation: A liquid crystalline approach. *Carbohydrate Research,* **328,** 165-176.

Wilkes, G. (2004). Corn, strange and marvelous: But is a definitive origin known. *Corn: Origin, History, Technology, and Production.* Hoboken**,** NJ, USA: John Wiley & Sons, Inc.

Youn, K.-S. & Chung, H.-S. (2012). Optimization of the roasting temperature and time for preparation of coffee-like maize beverage using the response surface methodology. *LWT - Food Science and Technology,* **46,** 305-310.

CHAPTER TWO

Chapter 2

Physicochemical, nutritional and antioxidant changes of heat-processed maize (*Zea mays* L.) grains – a review

Abstract

In developing countries most of the maize produced is consumed by humans as food. Maize processing is necessary to produce high quality, attractive, palatable and nutritious food products. To achieve these, maize must be heat-processed. Heat-processing affects the physicochemical, nutritional and antioxidant properties of maize used as raw material, intermediary ingredient or finished products. Processing of maize using heat ensures conversion of complex food substances into easily digestible compounds and reduction or removal of harmful microorganisms. Loss of nutrients, vitamins and production of off flavours due to decomposition of organic compounds by pyrolysis are some of the disadvantages of heat-processing. The use of superheated steam instead of dry heat significantly reduced the negative effects of heat-processing. This article reviewed heat-processing techniques of maize and their effects on physicochemical, nutritional and antioxidant properties of preprocessed and finished products.

Introduction

Maize (*Zea mays* L.), a cereal crop sometimes referred to as corn, originated about 7000 years ago in Mexico and developed into an important source of food by Native Americans (Ranum *et al.*, 2014). Maize is the most widely cultivated grain crop in the world with a total production of about 990 million metric tons (MMT) in 2014 (USDA, 2015a). The United States of America (USA) is the largest producer of maize with about 366 MMT in 2014 followed by China, Brazil, Ukraine and Mexico (Table 2.1). Most of the maize produced in developed countries is used for animal feed and as a raw material for processed food, pharmaceutical, confectionery and related industries. Approximately 40% of the maize produced in the USA is used for bio-ethanol production (Pollack, 2011). On the contrary, most of the maize produced in developing countries is consumed by humans as food. In Africa, maize contributes significantly as a staple human food. Maize kernels are typically white and yellow, but could, depending on the variety, also be blackish, bluish-grey, purple, green and red.

Table 2.1. Twenty countries with the largest maize production in 2014 (USDA, 2015a).

Country	Production (million metric tons)
USA	365,965
China	214,000
Brazil	75,000
Ukraine	27,000
Mexico	23,000
Argentina	23,500
India	21,000
South Africa	13,500
Russia	12,000
Canada	11,500
Indonesia	9,200
Philippines	7,900
Nigeria	7,500
Serbia	6,850
Ethiopia	6,500
Egypt	5,750
Vietnam	5,400
Tanzania	5,000
Pakistan	4,990
Thailand	4,990

Food processing is the conversion or transformation of raw ingredients into intermediate or finished products. The significance of food processing is to produce digestible, palatable, attractive and marketable food products from harvested crops or butchered animal meat. In addition, processing also ensures availability of food, reduces toxin contamination and makes it safe for consumption by killing pathogenic microorganisms and reducing the rate of spoilage. In order to make maize grain digestible and palatable for human consumption, heat-processing is required.

Maize is typically processed by means of boiling, nixtamalisation, extrusion and roasting (Bolade *et al.*, 2009). Heat-processing gelatinises the starch, making it easier for starch digesting enzymes to act on. Starch gelatinisation is induced by heating in the presence of water and results in organisational changes of starch granules (Waigh *et al.*, 2000). The starch granules absorb water, swell, lose crystallinity and leach amylose. This process is irreversible and required for desired functionality such as thickening and swelling of starch in a food system. Temperature of gelatinisation of starch is >50 °C and depends on the botanical source of the starch (Ratnayake & Jackson, 2006). Factors that affect gelatinisation of starch include rate of heating, moisture content, ratio of amylopectin to amylose, type of heat-processing method applied and starch source (Altay & Gunasekaran, 2006).

The physicochemical, nutritional and antioxidant properties of maize grains and products are affected by the heat-processing method. Many researchers have reported on the effects of various types of heat-processing methods on the physicochemical, nutritional, antioxidant content and properties of maize and maize products. The aim of this article is to review the importance of heat-processing methods applied to maize grain and their effects on the physicochemical, nutritional and antioxidant properties of preprocessed and finished products. Heat-processing techniques applied to maize such as nixtamalisation, extrusion and roasting will be overviewed with more emphasis on the later.

Maize kernel composition and properties

Composition

The major components of a maize kernel are the pericarp, endosperm, germ and tip cap (Fig. 2.1). The pericarp, also known as the hull or bran, is the outer layer which gives protection to the kernel against deterioration. It is made up of dietary fibre [hemicellulose (75%), cellulose (25%) and lignin (0.1%)] and phytochemicals (phenolics, phytic acids, tocotrienols, lignans and flavonoids) contributing health benefits. It accounts for 5% of the kernel and is undesirable to microorganisms and insects. Endosperm is the source of energy and protein for the germinating seed. It constitutes about 82% of the dry weight of the maize kernel. The starch in the endosperm is a polysaccharide, consisting of linear and helical amylose and branched-chain amylopectin. Normal maize contains about 27% linear

amylose polymer and 73% branched-chain amylopectin molecules (Erickson, 2006). Maize that contains only branched-chain amylopectin starch molecules (waxy maize) was genetically produced. Varieties of maize containing 70 – 82% linear chain amylose, called 'high amylose maize', have been genetically produced and commercialised. While the starch granules of waxy maize gelatinises like those of normal maize, the granules of high amylose maize cannot be gelatinised below 100 ºC. Starch granules of high amylose maize can only be gelatinised by pressure cooking in excess water at 110 – 120 ºC or hydration in dilute sodium hydroxide solution (Erickson, 2006). Endosperm also contains the protein prolamin known as zein. Zein contains high concentrations of leucine, alanine, proline and amides but is deficient in acidic (glutamate, aspartate) and basic (histidine, arginine, lysine) amino acids (Wall *et al.*, 1988; Burr & Burr, 1976). Maize varieties with nearly all hard endosperm are called 'flint' while those having nearly all soft endosperm are known as 'floury' and those that vary in the proportion of soft and hard endosperm are considered 'dent' (Pomeranz *et al.*, 1984).
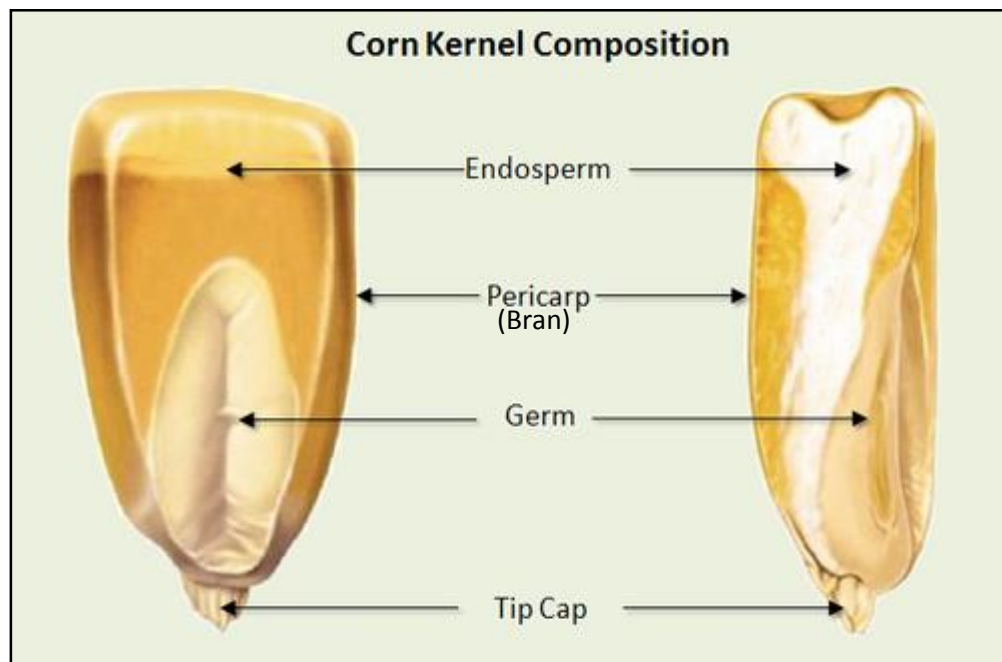
Figure 2.1. The four major components of a maize kernel. Reproduced with permission from Cereal Process Technologies, LLC. Overland Park, KS 66213 (CPT, 2015).

Germ is the living part and makes up about 12% of the maize kernel. It contains the essential genetic information, enzymes, vitamins and minerals for the kernel to grow into a maize plant. About 25% of the germ is oil which is the most valuable part of the maize kernel due to its content of unsaturated fat (linoleic acid) and bland taste. Tip cap is the area of the kernel not covered by the

pericarp. It is the major entry path for insects and water into the maize kernel and the point of attachment of the kernel to the cob. The primary objective of dry milling, an age-long processing method, of cereal grains is to separate the whole kernel into its anatomical components such as endosperm, germ and bran (Fig. 2.2). The endosperm can be used for producing different types of meals and flour for human consumption while the bran and germ are usually given to animals in their feed. This deprives humans from getting the benefit of bran and germ as sources of dietary fibre, antioxidants, protein, minerals and vitamins.
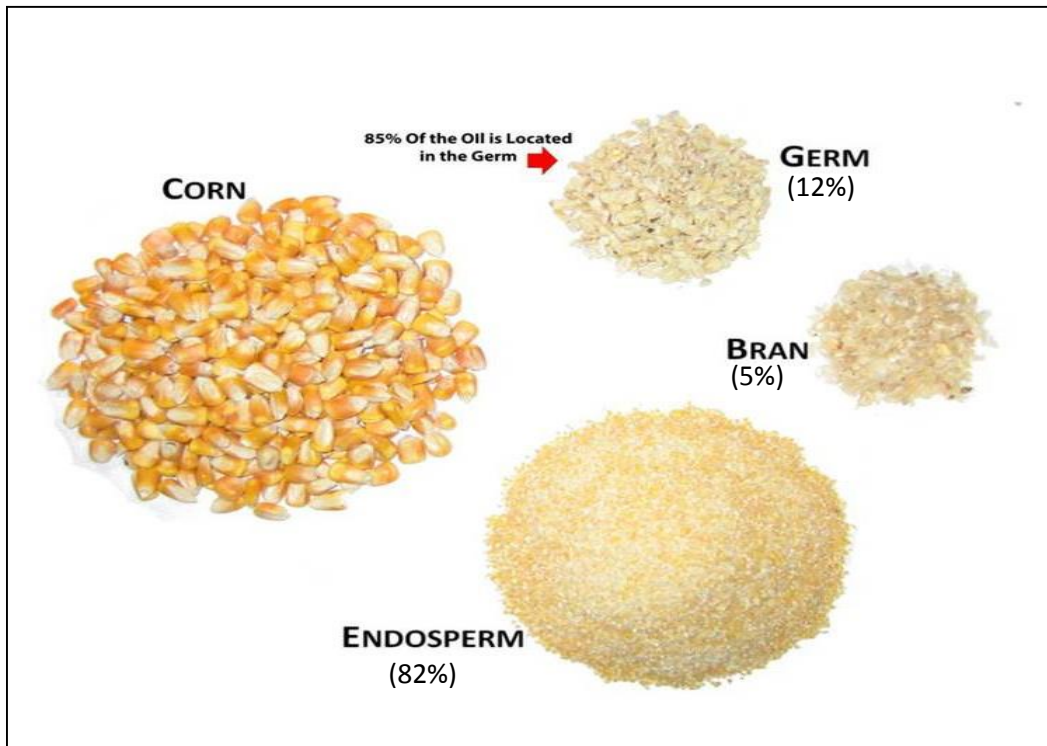
Figure 2.2. Primary products of maize kernel showing the germ, bran and endosperm fractions. Reproduced with permission from Cereal Process Technologies, LLC. Overland Park, KS 66213 (CPT, 2015).

Physicochemical properties

Physicochemical properties of maize grains are important to producers and processors involved in the trade and marketing of the grains and processed products worldwide. Kernel weight, kernel hardness, bulk density, colour, total soluble solids, pH, pasting temperature and viscosity are among the physicochemical properties of maize. Approximately 35 g was reported to be the average 100 kernel weight of maize grains (Chung *et al.*, 2011). Economically, maize kernel hardness is a very crucial trait to ensure the integrity of kernel during mechanical harvesting, storage and processing (Pratt *et al.*, 1995) and contributes to kernel bulk density (Dorsey-Redding *et al.*, 1990). Maize kernel bulk density

has been a grade-determining factor in the USA and many parts of the world. High temperature of roasting causes softening of texture, decomposition of insoluble polymers, production of Maillard reaction products and conversion of sugars to acidic compounds (Chung *et al.*, 2011). These are responsible for the changes the physicochemical properties of roasted maize.

Nutritional properties

Nutrients in food provide consumers with energy, minerals and vitamins for proper functioning of the body. Crude protein, dietary fibre, carbohydrate, oil, amino acids, minerals and vitamins are among the nutritional properties of maize grains, preprocessed and finished products. Whole maize grain contains approximately 72% starch (carbohydrate), 10% protein, 4% oil and has energy density of about 365 kcal/100 g (Ranum *et al.*, 2014). It is a source of the essential elements magnesium and phosphorus in moderate quantity and others like zinc, iron, potassium, sodium and manganese in trace amount. Riboflavin (0.20 mg/100 g), thiamine (0.39 mg/100 g) vitamin B_6 (0.62 mg/100 g) and niacin (3.63 mg/100 g) are the most important vitamins available in maize grains (USDA, 2015b). The saturated fatty acids content of maize grains is very low (0.67 g/100 g), it contains high amount of mono- and poly-unsaturated fatty acids (3.41 g/100 g) and is completely free of cholesterol.

Maize grains contain considerable quantity of the essential amino acids threonine, isoleucine, leucine, phenylalanine, tyrosine and valine but are very low in lysine and tryptophan (FAO, 2013). Providing at least one fifth of the total daily energy, maize supplies a total daily protein intake for 17 to 60% of the people in 12 African countries (Krivanek *et al.*, 2007). For a balanced nutrition, any maize-based diet must be complemented with a high source of the essential amino acids lysine and tryptophan such as pulses, meat and dairy products (Vivek, 2008). Maize varieties with high lysine and tryptophan content, known as quality protein maize (QPM), were developed by breeders at the International Maize and Wheat Improvement Center (CIMMYT) in Mexico with the aim of reducing deficiency of the two essential amino acids in the affected areas worldwide (Krivanek *et al.*, 2007).

Antioxidant properties

Whole grain cereals contain health promoting phytochemicals such as phenolic compounds with high antioxidant activities (Dykes & Rooney, 2007). Phenolic acids, flavonoids, anthocyanins and carotenoids are among the phytochemicals with antioxidant properties available in maize grains. Antioxidants are organic compounds that retard or inhibit the autoxidation of free radicals. Free radicals are highly reactive atoms or molecules containing one or more unpaired electrons (Valko *et al.*, 2006). The high reactivity of free radicals results in chain reactions responsible for damaging proteins, DNA, lipids and carbohydrates in body cells (Halliwell *et al.*, 1992). This damage eventually causes cell injury, cell death, increase in aging process and diseases such as cardiovascular disorders, cancers and diabetes mellitus (Wong *et al.*, 1999).

Human systems have natural antioxidants defence mechanism that neutralises the effects of free radicals. These include antioxidant enzymes that are synthesised in the body and antioxidant nutrients that are available in food which convert the free radicals into neutral and harmless substances that can be excreted (Oboh, 2005). Consumption of foods (especially whole grains) and beverages containing phenolic compounds may have the ability of minimising the risk of heart diseases and certain cancers. The activity of phenolic compounds as antioxidants is as a result of their redox properties that make them serve the function of reducing agents, singlet oxygen quenchers, metal chelators and hydrogen donors (Rice-Evans *et al.*, 1997).

Heat-processing of maize grains

Heat-processing have different effects on the physicochemical, nutritional and antioxidant properties of maize grains, intermediary and finished food products. The choice of method for heat-processing depends on ingredients, environment, economy and traditions of people. Typical heat-processing methods of maize include nixtamalisation (lime cooking), extrusion, roasting, boiling, steaming and baking. For the purpose of this review, the first three methods were considered with more emphasis on roasting.

Nixtamalisation

Nixtamalisation, a heat-processing method also known as lime cooking, is the cooking of maize grains in various concentrations (0.3 – 2.0 g/100 g) of calcium hydroxide ($Ca(OH)_2$) solutions, steeping for 12 to 16 h, washing and grinding to obtain masa (maize dough) and flour (Salazar *et al.*, 2014). During the process of nixtamalisation, influence of cooking temperature, concentration of $Ca(OH)_2$ (lime) and agitation results in simultaneous diffusion of water and calcium into the maize kernels leading to physical, chemical, nutritional and organoleptic changes in the products (Quintanar Guzmán *et al.*, 2009; Pappa *et al.*, 2010).

Advantages of nixtamalisation include facilitation of milling, improvement of protein quality, increasing concentrations of niacin (nicotinic acid or vitamin B_3) and calcium and decreasing mycotoxin content. Removal of maize bran and germ, reducing the content of dietary fibre and loss of carotenoids and other vitamins are the major disadvantages of nixtamalisation (Bressani *et al.*, 2004; Salazar *et al.*, 2014). Extensive research was conducted over the years on the effect of nixtamalisation on the physicochemical, nutritional and antioxidant properties of different varieties of maize, including QPM, and other crops some of which are summarised in Table 2.2. Temperature of 85 °C, ratio of grain-to-cooking medium of 1:3 (w/v), cooking time of 31 min, lime concentration of 5.4 g/L and steeping time of 8.1 h were reported as the optimum nixtamalisation condition of QPM for production of nixtamalised flour (Milán-Carrillo *et al.*, 2004).

Table 2.2. Effect of nixtamalisation on physicochemical, nutritional and antioxidant properties of maize and maize products.

Process variable	Kernel colour	Effect	Reference
		Physicochemical	
Maize/water ratio and cooking temperature	White	Significantly reduced gelatinisation temperature of extrudates	Ruiz-Gutiérrez *et al.* (2010)
Different calcium sources and temperature	Blue	Colour decreased with increase in calcium hydroxide concentration while increase in calcium lactate has opposite effect	Sánchez-Madrigal *et al.* (2014)
Added lime concentration and temperature	Not specified	Acrylamide content decreased with an increase in lime concentration	Arámbula-Villa *et al.* (2007)
Lime concentration and temperature	Not specified	Larger granules observed in nixtamalised starch than in raw starch and increase in temperature reduced starch retrogradation	Méndez-Montealvo *et al.* (2008)
Cooking temperature and time	Not specified	Formation of calcium cluster and apparition of micro-holes for calcium uptake by the endosperm were observed	Valderrama-Bravo *et al.* (2010)
Lime concentration, wood ash and temperature	White	Higher amount of soluble solids in lime liquor (2.4%) than in wood ash liquor (1%)	Pappa, de Palomo and Bressani (2010)
Cooking time, lime concentration and temperature	Not specified	Cooking time and lime concentration significantly affected colour and pH whereas paste viscosity was not affected	Sefa-Dedeh *et al.* (2004)
Polymerisation changes in maize proteins, cooking time	Not specified	Thermal transitions occurred between 55 and 62 ºC which probably corresponds to starch	Guzmán *et al.* (2010)

and temperature		retrogradation of the extrudates	
Lime concentration, cooking time and temperature	White and yellow QPM	Extractable albumins and globulins of QPM products were higher than those of regular maize	Vivas-Rodriguez *et al.* (1990)

Nutritional

Maize/water ratio, temperature and agitation	White	Cooking temperature significantly affect water and calcium absorption of the grains	Ruiz-Gutiérrez *et al.* (2010)
Cooking time, lime concentration and temperature	Not specified	Lime concentration did not significantly affect protein and ash content of the products	Sefa-Dedeh *et al.* (2004)
Cooking temperature and time	Not specified	Calcium uptake significantly increased in the pericarp with increase in temperature	Valderrama-Bravo *et al.* (2010)
Grain structure and cooking temperature	Not specified	No improvement in *in vitro* protein digestibility in cooked and uncooked maize	Duodu *et al.* (2002)
Lime concentration, wood ash and temperature	White	Protein quality of the two alkali cooked products was lower than that of raw maize	Pappa *et al.* (2010)

Antioxidants

Food grade lime, cooking temperature and time	White, yellow, black, blue, red and purple	Yellow and purple maize varieties showed the highest nitric oxide scavenging capacity among the maize varieties studied	López-Martínez *et al.* (2012)
Different calcium sources and cooking temperature	Blue	Anthocyanins, total phenolics and antioxidant activity decreased with increase in calcium hydroxide concentration but increased with decrease in calcium lactate	Sánchez-Madrigal *et al.* (2014)
Concentrations of calcium hydroxide	Blue	Total anthocyanins content decreased with an increase in	Cortés *et al.* (2006)

and temperature		calcium hydroxide concentration	
Cooking temperature and time	White and blue	Mexican blue maize showed lower total polyphenolic content and higher antioxidant activity compared to the white maize	Del Pozo-Insfran *et al.* (2006)
Sodium hydroxide concentration, time, temperature and agitation	White	Total phenolics, hydroxycinnamic acid concentration and antioxidant capacity varied with respect to the type of maize fibre	Ayala-Soto *et al.* (2014)

Extrusion

Extrusion is defined as a quick heat-processing technique which uses high temperature and pressure and short time (Sharma *et al.*, 2012). The process of extrusion subjects food materials to an intense mechanical shear. Extrusion could be used for the preparation of various preprocessed and processed maize food products such as breakfast cereals, baby complementary foods, snacks and pet foods. Generally, moistened starchy or proteinaceous foods are transformed into viscous, plastic-like dough and cooked prior to being forced through the extruder die (Lazou & Krokida, 2010). Extruded foods have consumer preference because of their attractive appearance, good texture and convenience in addition to containing useful bioactive components. Other properties of extruded foods such as water solubility index (WSI), water absorption capacity (WAC), bulk density, dough viscosity, oil absorption index and expansion index determine their particular application (Hernández-Díaz *et al.*, 2007).

The desirable effects of extrusion on nutritional value include starch gelatinisation and destruction of antinutritional factors and toxins (Singh *et al.*, 2007). Loss of heat-labile vitamins and reduction of amino acids through non-enzymatic browning caused by Maillard reactions between amino acids of protein and sugars of carbohydrate are some of the undesirable effects of extrusion (Ilo & Berghofer, 2003). Quality of extrudates always depends largely on the type of extruder, moisture content of raw material, screw speed, barrel temperature, feed rate and screw configuration of the extruder (Ding *et al.*, 2005). Comprehensive reviews on extrusion have been published which include effects of extrusion cooking on nutritional values (Björck & Asp, 1983; Singh *et al.*, 2007), retention of flavour of extrudates during high temperature short time extrusion cooking (Bhandari *et al.*, 2001), fate of mycotoxins during extrusion cooking of cereals (Castells *et al.*, 2005), vitamins stability during extrusion cooking (Riaz *et al.*, 2009), functionality of polysaccharides through extrusion cooking (Wolf, 2010), effects of extrusion on bioactive compounds and their antioxidant activities in foods (Brennan *et al.*, 2011), data compilation of WAC and WSI of extruded food products (Oikonomou & Krokida, 2011).

Table 2.3 summarises the effects of extrusion cooking on some physicochemical, nutritional and antioxidant properties of maize extruded products. The optimum extrusion conditions of QPM flour for the production of tortilla were reported to be 85 °C, 0.21% (w/w) lime concentration and 240 rpm screw speed using a single screw extruder (Milán-Carrillo *et al.*, 2006).

Table 2.3. Effect of extrusion cooking on physicochemical, nutritional and antioxidants properties of maize products.

Raw material	Extrusion condition	Effect	Reference
		Physicochemical	
Maize flour, olive oil and broccoli	Screw speed and extrusion temperature	Increase in olive oil or broccoli paste and decrease in extrusion temperature produced denser extrudates with low porosity	Bisharat *et al.* (2013)
Maize grits	Feed rate, extrusion temperature, feed moisture	Increase in moisture decreased viscosity, gelatinisation and radial expansion ratio resulting in extrudates with higher density	Ilo *et al.* (1996)
Maize grits and maize fibre mixture	Melt temperature and CO_2 injection	At lower temperature the surface of CO_2 injected extrudates were smooth with low fracturability. Opposite effects were observed with increase in maize fibre	Wang and Ryu (2013a)
Maize flour and maize flour/lentil mixture	Feed rate, feed moisture and extrusion temperature	WAC of extrudates increased with increase in temperature and moisture but decreased with decrease in feed rate and maize/lentil ratio	Andriana Lazou and Krokida (2010)
Maize starch, whey protein concentrate and *Agave tequilana* fibre	Screw compression ratio, die nozzle and barrel temperature	Increase in fibre decreased lightness, total colour difference and greenness of the extrudates	Santillán-Moreno *et al.* (2011)
High amylose	Screw speed and	Increase in screw speed increased	Zhu *et al.* (2010)

maize starch and soy protein concentrate (SPC)	SPC level	WSI, WAC and expansion ratio and decreased bulk density, while increase in SPC increased bulk density and decreased WAC and expansion ratio of extrudates	
Maize grits	Die pressure, screw torque, feed moisture and temperature	Disruption of maize grit particles and their starch granules was observed and complex crystalline amylose – lipid complex occurred	Ollett *et al.* (1990)
		Nutritional	
Maize grits	Moisture, speed and temperature	Significant loss of lysine, arginine as well as cysteine was observed	Ilo and Berghofer (2003)
QPM and commercial nixtamalised MASECA flours	Screw length/ diameter ratio, die opening and temperature	Extruded QPM flour showed higher protein, lysine contents, total and resistant starch contents than those of nixtamalised MASECA flour	Gutiérrez-Dorado *et al.* (2008)
Maize, whey protein concentrate and *Agave tequilana* fibre	Screw compression ratio, die nozzle, pH and barrel temperature	Extrudates with high fibre and alkaline pH gave the highest insoluble and total dietary fibre	Santillán-Moreno *et al.* (2011)
QPM grits and flours	Lime concentration, water, temperature and time	Protein digestibility of the QPM extrudates decreased from 79.05% to between 74.30 and 78.30%	Milán-Carrillo *et al.* (2006)
		Antioxidants	
Mixed maize grits and fibre	Mass ratio and melt temperature	Increase in maize fibre decreased loss of phenolics and increased antioxidant activities	Wang and Ryu (2013b)
Maize grits and yam flour	Feed rate, speed and temperature	Antioxidant activities increased and remained unaffected depending on	Chiu *et al.* (2012)

mixture		the assay used	
Maize fine grits	Feed rate, lime concentration and temperature	Total phenolics content and antioxidant activity of the extrudates decreased significantly	Aguayo-Rojas *et al.* (2012)
Blue maize grits and flour	Lime concentration, temperature and feed rate	Extrudates lost >55% of anthocyanins but higher percentage of ferulic acids was retained	Mora-Rochin *et al.* (2010)
Maize and bean flour	Feed moisture and temperature	Total polyphenols, flavonoids and antioxidant activities of the extrudates decreased with an increase in temperature	Delgado-Licon *et al.* (2008)

Roasting

Roasting is a processing technique that makes use of dry heat. It increases the shelf life of foods and enhances the efficiency of subsequent processing steps (Asep *et al.*, 2008; Cämmerer & Kroh, 2009). Processing of maize grains by roasting results in changes of the chemical composition, flavour and physical properties. Information obtained on the changes in physicochemical, nutritional and antioxidant properties can be used to improve on the quality of products developed.

The extent of grain roasting can be observed through the changes that occur in the physicochemical characteristics of the raw grain during roasting. Increase in roasting temperature and time results in decreased weight retention of maize kernels (Chung *et al.*, 2011). This is attributed to loss in moisture content due to evaporation during roasting. It may also be as a result of differences in inner vapour pressure that developed in the maize kernels by the roasting conditions. Bulk density of maize kernels also decreases as roasting temperature and time increase. This finding was similar to that of Pittia *et al.* (2001) whom reported that the reason may be because of changes in pattern of moisture loss and gain in volume of the roasted maize kernels. Jha (2005) further clarifies that changes in bulk density of grains during roasting are as a result of internal pores development, expansion, loss of moisture and changes in cellular structure. The reduction in bulk density of roasted maize was similar to those reported in hazelnuts (Saklar *et al.*, 2003) and wheat (Murthy *et al.*, 2008). There was no significant change in soluble solids content of the maize kernels roasted at temperatures between 160 and 180 °C for 50 min (Chung *et al.*, 2011). However, *Chung et al.* (2011) found that soluble solids content significantly increased after roasting maize kernels for 30 min at

temperatures of 200, 220 and 240 °C. Softening of texture for influx of materials and insoluble polymer decomposition due to high roasting temperature are responsible for increase in total soluble solids (Kahyaoglu & Kaya, 2006). Increase in roasting temperature and time leads to decrease in pH of maize kernels (Chung *et al.*, 2011). Park *et al.* (1993) reported that decrease in pH caused by high roasting temperature is due to conversion of sugars into acidic compounds and generation of Maillard reaction products.

Increase in temperature and time of roasting decreased the protein digestibility of maize grains and increase in roasting time showed more variation than increase in roasting temperature (Srivastav *et al.*, 1990). Roasting maize grains for 17 min at temperatures between 120 and 130 °C caused significant increase in total carbohydrate, crude fat and the minerals (sodium, calcium, zinc and magnesium) whereas crude fibre and protein, potassium and iron contents significantly decreased (Oboh *et al.*, 2010). The total carbohydrate content of plant materials is obtained by difference therefore, increase of the former could be due to decrease in crude protein, fibre and moisture contents of the roasted maize grains. Roasting might have increased the crude fat content of the roasted maize grains by thermal break down of bonds between fat and matrix of the maize leading to release of reserved oil, while decrease in fibre and protein could be associated to depolymerisation of fibre molecules and Maillard reactions, respectively (Oboh *et al.*, 2010). Even though they reported significant changes in mineral elements of roasted maize grain, the possible reasons were not highlighted and remain largely unknown.

Roasting process caused increase in the content and activity of antioxidants, brown colouration and enhanced flavour of end-products due to the presence of Maillard reaction products (MRPs) (Lee & Lee, 2009). These changes contribute to better health benefits through enhancing the digestibility of nutrients and activity of available antioxidants (Dewanto *et al.*, 2002; Jaramillo-Flores *et al.*, 2003). Summa *et al.* (2006) reported that MRPs are formed as a result of high heat treatment, have molecular weights of less than 30 kDa and their antioxidant activity is strong. The influence of roasting on the antioxidant activity of small black soybean (SBS) indicated that roasted SBS contains higher amount of phenolics compared to unroasted SBS and the same pattern was observed in the result of radical scavenging assay (Kim *et al.*, 2011). The researchers suggested that the observed increase in phenolics content was as a result of increase in the release of phytochemicals as phenolic acids from the matrices of SBS cells. Disruption of cell wall and cell membrane due to thermal processing of grains is responsible for the release of soluble phenolics from the bonds of insoluble esters (Dewanto *et al.*, 2002). They also reported that an increased quantity of solubilised ferulic acid (a phenolic acid) in roasted maize results in increase in total antioxidant activity which occurs significantly only at temperatures above 180 °C. Similar pattern for phenolics content in SBS at temperatures between 150 and 250 °C was reported (Kim *et al.*, 2011). Oboh *et al.* (2010) corroborated decrease in the

content of extractible phenolics and flavonoids, and increase in antioxidant capacity of roasted white and yellow maize.

Other effects of roasting conditions on the physicochemical, nutritional and antioxidant properties of maize and maize products are summarised in Table 2.4. The optimum roasting time and temperature of Korean maize varieties for the production coffee-like beverage using extraction yield, free sugar and phenolic compounds content and antioxidant activities as response variables were found to be 24 min and 207 °C, respectively (Youn & Chung, 2012).

Table 2.4. Effect of roasting conditions on physicochemical, nutritional and antioxidants properties of maize and maize products

Maize/maize product	Roasting condition	Type of roaster	Effect	Reference
			Physicochemical	
Maize grains and maize native starch	Temperature (20 – 120 °C) and time (20 – 180 min)	Laboratory fluidised-bed dryer	High temperature reduced the swelling capacity of starch granules but increased starch gelatinization	Malumba *et al.* (2010)
Maize grains	Temperature (80 – 160 °C)	LP-gas-fired roasting machine	Test weight decreased and gelatinization increased with increase in roasting temperature	Costa *et al.* (1977)
Maize grains	Temperature (160 – 240 °C) and time (10 – 50 min)	Electric rotary roaster (DR-1)	Extraction yield increased while free sugar decreased in the roasted maize beverage with increase in temperature and time	Youn and Chung (2012)
			Nutritional	
Maize grains	Temperature (50 – 130 °C) and time (14 – 17 min)	Aluminium frying pan with electric stove (100W)	No significant changes in proximate composition whereas vitamins B_1 and B_2, isoleucine and lysine contents decreased	Ayatse *et al.* (1983)
Maize grains	Temperature (110 – 140 °C)	Liquid propane fired roaster (Roast-A-Matic®)	Dry matter decreased while protein content increased in the roasted maize grains	Hamilton and Thompson (1992)

Maize grains	Temperature (80 – 160 °C)	LP-gas-fired roasting machine	No significant effect on protein, lysine, ash, lipid, acid detergent fibre contents and gross energy with increase in temperature	Costa *et al.* (1977)
			Antioxidants	
Dried and fresh maize grains	Sand bath roasting	Sand bath (local roasting)	Phytic acids content decreased by 23.7% and 46.7% for dried and fresh maize grains, respectively	Khan *et al.* (1991)
Maize grains	Temperature (160 – 240 °C) and time (10 – 50 min)	Electric rotary roaster (DR-1)	Content of phenolic compounds increased with increase in temperature and time of roasting	Chung *et al.* (2011)
Maize grains	Temperature (160 – 240 °C) and time (10 – 50 min)	Electric rotary roaster (DR-1)	Phenolic compounds and antioxidant activities of the grains increased with increase in temperature and time	Youn and Chung (2012)

Emerging technology of heat-processing of maize

A new roasting technology known as forced convection roasting (FCR) shows promise in terms of addressing the disadvantages of dry heat-processing of maize grains due to the option of using superheated steam (dry steam). FCR is a novel processing technique in which superheated steam is forced through the grains while continuously being mixed and moving through the roasting chamber of a forced convection continuous tumble roaster (FCCTR). The superheated steam and continuous tumbling of grains in the roasting chamber result in even and faster heat transfer in the grains ensuring uniform roasting (Fritz, 2013). Marama bean (*Tylosema esculentum*) was dry-heated (roasted) using FCCTR (model not specified) (Roastech, Bloemfontein, South Africa) for 20 min at 150 ⁰C (Maruatona *et al.*, 2010). The result indicated significant increase in *in vitro* protein digestibility and water absorption capacity, and reduction in protein solubility and emulsifying capacity of the marama bean flour. The heated marama bean flours (full fat and defatted) were used in composite with sorghum flour for the preparation of porridge (Kayitesi *et al.*, 2010; Kayitesi *et al.*, 2012). The composite porridge of the full fat flour had a flavour of roasted nut and was more acceptable to consumers compared to that of the defatted flour. Nyembwe *et at.* (2015) roasted marama beans at 150 ⁰C using

FCCTR (model not specified) and determined the total phenolics content, phenolic composition, saponin content and sensory attribute of the water extracts. Their result showed that roasting of the marama beans for more than 20 min caused bitterness of the end product and was attributed to the identified phenolic acids, saponins and other unidentified compounds. The negative effect reported might be due to the use of dry heat instead of superheated steam for the roasting.

However, a study conducted to investigate the effect of FCR on the physicochemical and antioxidant properties, and optimisation of roasting conditions of maize varieties using FCCTR, model R100E (Roastech, Bloemfontein, South Africa) did not result in negative effects (Chapters 3 and 4). Roasting temperature and speed limits used were 150 to 220 ºC and 20 to 90 Hz, respectively. The FCCTR used required the tempering (increase in moisture content) of the maize kernels to a value between 18 and 20 % prior to roasting. The high moisture content of the tempered maize kernels resulted in generation of superheated steam that replaced the dry hot air during roasting. Nutritional quality and antioxidant properties of the roasted maize were not significantly affected due to use of superheated steam.

Conclusion

Most heat-processing methods of maize produce intermediary products which can easily be further transformed into ready-to-eat, digestible, palatable, healthy and nutritious food products. The advantages of heat-processing of maize include the reduction or removal of harmful microorganisms and toxins, and conversion of complex food substances into easily digestible and ingestible food products. Loss of nutrients (such as dietary fibre and amino acids), vitamins (especially soluble and heat-labile) and production of off flavours as a result of decomposition of organic compounds due to pyrolysis are the most important disadvantages of heat-processing of maize. Nixtamalisation involves the removal of maize bran, maize germ and generation of large quantity of effluent. Extrusion cooking results in intense mechanical shear on the products. Furthermore, roasting of maize grains using dry heat in conventional roasting equipment causes decomposition of organic substances. These contribute to the negative effects on the quality of products highlighted above. Therefore, forced convection roasting of tempered grains could be considered as a promising heat-processing method for the production of foods with high nutritional quality.

References

Aguayo-Rojas, J., Mora-Rochín, S., Cuevas-Rodríguez, E., Serna-Saldivar, S., Gutierrez-Uribe, J., Reyes-Moreno, C. & Milán-Carrillo, J. (2012). Phytochemicals and antioxidant capacity of tortillas obtained after lime-cooking extrusion process of whole pigmented mexican maize. *Plant Foods for Human Nutrition,* **67,** 178-185.

Altay, F. & Gunasekaran, S. (2006). Influence of drying temperature, water content, and heating rate on gelatinization of corn starches. *Journal of Agricultural and Food Chemistry,* **54,** 4235-4245.

Arámbula-Villa, G., Gutiérrez-Árias, E. & Moreno-Martínez, E. (2007). Thermal properties of maize masa and tortillas with different components from maize grains, and additives. *Journal of Food Engineering,* **80,** 55-60.

Asep, E., Jinap, S., Tan, T.J., Russly, A., Harcharan, S. & Nazimah, S. (2008). The effects of particle size, fermentation and roasting of cocoa nibs on supercritical fluid extraction of cocoa butter. *Journal of Food Engineering,* **85,** 450-458.

Ayala-Soto, F.E., Serna-Saldívar, S.O., García-Lara, S. & Pérez-Carrillo, E. (2014). Hydroxycinnamic acids, sugar composition and antioxidant capacity of arabinoxylans extracted from different maize fiber sources. *Food Hydrocolloids,* **35,** 471-475.

Ayatse, J.O., Eka, O.U. & Ifon, E.T. (1983). Chemical evaluation of the effect of roasting on the nutritive value of maize (*Zea mays* Linn.). *Food Chemistry,* **12,** 135-147.

Bhandari, B., D'arcy, B. & Young, G. (2001). Flavour retention during high temperature short time extrusion cooking process: A review. *International Journal of Food Science and Technology,* **36,** 453-461.

Bisharat, G.I., Oikonomopoulou, V.P., Panagiotou, N.M., Krokida, M.K. & Maroulis, Z.B. (2013). Effect of extrusion conditions on the structural properties of corn extrudates enriched with dehydrated vegetables. *Food Research International,* **53,** 1-14.

Björck, I. & Asp, N.G. (1983). The effects of extrusion cooking on nutritional value — a literature review. *Journal of Food Engineering,* **2,** 281-308.

Bolade, M.K., Adeyemi, I.A. & Ogunsua, A.O. (2009). Influence of particle size fractions on the physicochemical properties of maize flour and textural characteristics of a maize-based nonfermented food gel. *International Journal of Food Science and Technology,* **44,** 646-655.

Brennan, C., Brennan, M., Derbyshire, E. & Tiwari, B.K. (2011). Effects of extrusion on the polyphenols, vitamins and antioxidant activity of foods. *Trends in Food Science and Technology,* **22,** 570-575.

Bressani, R., Turcios, J.C., Colmenares De Ruiz, A.S. & De Palomo, P.P. (2004). Effect of processing conditions on phytic acid, alcium, iron, and zinc contents of lime-cooked maize. *Journal of Agricultural and Food Chemistry,* **52,** 1157-1162.

Burr, B. & Burr, F.A. (1976). Zein synthesis in maize endosperm by polyribosomes attached to protein bodies. *Proceedings of the National Academy of Sciences,* **73,** 515-519.

Cämmerer, B. & Kroh, L.W. (2009). Shelf life of linseeds and peanuts in relation to roasting. *LWT-Food Science and Technology,* **42,** 545-549.

Castells, M., Marin, S., Sanchis, V. & Ramos, A.J. (2005). Fate of mycotoxins in cereals during extrusion cooking: A review. *Food Additives and Contaminants,* **22,** 150-157.

Chiu, H.-W., Peng, J.-C., Tsai, S.-J. & Lui, W.-B. (2012). Effect of extrusion processing on antioxidant activities of corn extrudates fortified with various chinese yams (*Dioscorea sp.*). *Food and Bioprocess Technology,* **5,** 2462-2473.

Chung, H.-S., Chung, S.-K. & Youn, K.-S. (2011). Effects of roasting temperature and time on bulk density, soluble solids, browning index and phenolic compounds of corn kernels. *Journal of Food Processing and Preservation,* **35,** 832-839.

Cortés, G.A., Salinas, M.Y., Martín-Martinez, E.S. & Martínez-Bustos, F. (2006). Stability of anthocyanins of blue maize (*Zea mays* L.) after nixtamalization of seperated pericarp-germ tip cap and endosperm fractions. *Journal of Cereal Science,* **43,** 57-62.

Costa, P., Jensen, A., Harmon, B. & Norton, H. (1977). Effects of roasting and roasting temperatures on the nutritive value of high-moisture corn for swine. *Journal of Animal Science,* **44,** 234-241.

CPT (2015). Corn kernel composition. Cereal Process Technologies. URL: http://www.cerealprocess.com/fractionation/ Accessed 01/June/2015.

Del Pozo-Insfran, D., Brenes, C.H., Serna Saldivar, S.O. & Talcott, S.T. (2006). Polyphenolic and antioxidant content of white and blue corn (*Zea mays* L.) products. *Food research international,* **39,** 696-703.

Delgado-Licon, E., Ayala, A.L.M., Rocha-Guzman, N.E., Gallegos-Infante, J.-A., Atienzo-Lazos, M., Drzewiecki, J., Martínez-Sánchez, C.E. & Gorinstein, S. (2008). Influence of extrusion on the bioactive compounds and the antioxidant capacity of the bean/corn mixtures. *International Journal of Food Science and Nutrition,* **60,** 522-532.

Dewanto, V., Wu, X. & Liu, R.H. (2002). Processed sweet corn has higher antioxidant activity. *Journal of Agricultural and Food Chemistry,* **50,** 4959-4964.

Ding, Q.-B., Ainsworth, P., Tucker, G. & Marson, H. (2005). The effect of extrusion conditions on the physicochemical properties and sensory characteristics of rice-based expanded snacks. *Journal of Food Engineering,* **66,** 283-289.

Dorsey-Redding, C., Hurburgh, C., Johnson, L.A. & Fox, S.R. (1990). Adjustment of maize quality data for moisture content. *Cereal Chemistry,* **67,** 292-295.

Duodu, K.G., Nunes, A., Delgadillo, I., Parker, M.L., Mills, E.N.C., Belton, P.S. & Taylor, J.R.N. (2002). Effect of grain structure and cooking on sorghum and maize in vitro protein digestibility. *Journal of Cereal Science,* **35,** 161-174.

Dykes, L. & Rooney, L. (2007). Phenolic compounds in cereal grains and their health benefits. *Cereal Foods World,* **52,** 105-111.

Erickson, A. (2006). *Corn starch.* Pp. 1-41. Washington, DC, USA: Corn Refiners Association.

FAO (2013). FAO corporate document repository. Food and Agriculture Organisation. URL: http://www.fao.org/docrep/t0395e/T0395E02.htm#World%20production Accessed 02/June/2015.

Fritz, T. (2013). Backgound and working principle (operation manual) of forced convection continuous tumble roaster (FCCTR). Roastech, Bloemfontein, South Africa.

Gutiérrez-Dorado, R., Ayala-Rodríguez, A., Milán-Carrillo, J., López-Cervantes, J., Garzón-Tiznado, J., López-Valenzuela, J., Paredes-López, O. & Reyes-Moreno, C. (2008). Technological and nutritional properties of flours and tortillas from nixtamalized and extruded quality protein maize (*Zea mays* L.). *Cereal Chemistry,* **85,** 808-816.

Guzmán, A.Q., Jaramillo Flores, M.E., Feria, J.S., Méndez Montealvo, M.G. & Wang, Y.-J. (2010). Effects of polymerization changes in maize proteins during nixtamalization on the thermal and viscoelastic properties of masa in model systems. *Journal of Cereal Science,* **52,** 152-160.

Halliwell, B., Gutteridge, J. & Cross, C.E. (1992). Free radicals, antioxidants, and human disease: Where are we now? *The Journal of Laboratory and Clinical Medicine,* **119,** 598-620.

Hamilton, R.M. & Thompson, B.K. (1992). Chemical and nutrient content of corn (*Zea mays*) before and after being flame roasted. *Journal of the Science of Food and Agriculture,* **58,** 425-430.

Hernández-Díaz, J., Quintero-Ramos, A., Barnard, J. & Balandran-Quintana, R. (2007). Functional properties of extrudates prepared with blends of wheat flour/pinto bean meal with added wheat bran. *Food Science and Technology International,* **13,** 301-308.

Ilo, S. & Berghofer, E. (2003). Kinetics of lysine and other amino acids loss during extrusion cooking of maize grits. *Journal of Food Science,* **68,** 496-502.

Ilo, S., Tomschik, U., Berghofer, E. & Mundigler, N. (1996). The effect of extrusion operating conditions on the apparent viscosity and the properties of extrudates in twin-screw extrusion cooking of maize grits. *LWT - Food Science and Technology,* **29,** 593-598.

Jaramillo-Flores, M., Gonzalez-Cruz, L., Cornejo-Mazon, M., Dorantes-Alvarez, L., Gutiérrez-López, G. & Hernández-Sánchez, H. (2003). Effect of thermal treatment on the antioxidant activity and content of carotenoids and phenolic compounds of cactus pear cladodes (*Opuntia ficus-indica*). *Food Science and Technology International,* **9,** 271-278.

Jha, S. (2005). Mathematical simulation of roasting of grain. *Journal of Food Engineering,* **71,** 304-310.

Kahyaoglu, T. & Kaya, S. (2006). Modeling of moisture, color and texture changes in sesame seeds during the conventional roasting. *Journal of Food Engineering,* **75,** 167-177.

Kayitesi, E., De Kock, H.L., Minnaar, A. & Duodu, K.G. (2012). Nutritional quality and antioxidant activity of marama–sorghum composite flours and porridges. *Food Chemistry,* **131,** 837-842.

Kayitesi, E., Duodu, K.G., Minnaar, A. & De Kock, H.L. (2010). Sensory quality of marama/sorghum composite porridges. *Journal of the Science of Food and Agriculture,* **90,** 2124-2132.

Khan, N., Zaman, R. & Elahi, M. (1991). Effect of heat treatments on the phytic acid content of maize products. *Journal of the Science of Food and Agriculture,* **54,** 153-156.

Kim, H.G., Kim, G.W., Oh, H., Yoo, S.Y., Kim, Y.O. & Oh, M.S. (2011). Influence of roasting on the antioxidant activity of small black soybean (*Glycine max* L. Merrill). *LWT - Food Science and Technology,* **44,** 992-998.

Krivanek, A.F., De Groote, H., Gunaratna, N.S., Diallo, A. & Friesen, D. (2007). Breeding and disseminating quality protein maize (QPM) for africa. *African Journal of Biotechnology,* **6,** 312-324.

Lazou, A. & Krokida, M. (2010). Functional properties of corn and corn–lentil extrudates. *Food Research International,* **43,** 609-616.

Lee, S. & Lee, J. (2009). Effects of oven-drying, roasting, and explosive puffing process on isoflavone distributions in soybeans. *Food Chemistry,* **112,** 316-320.

López-Martínez, L.X., Parkin, K.L. & Garcia, H.S. (2012). Effect of processing of corn for production of masa, tortillas and tortilla chips on the scavenging capacity of reactive nitrogen species. *International Journal of Food Science and Technology,* **47,** 1321-1327.

Malumba, P., Janas, S., Roiseux, O., Sinnaeve, G., Masimango, T., Sindic, M., Deroanne, C. & Béra, F. (2010). Comparative study of the effect of drying temperatures and heat-moisture treatment on the physicochemical and functional properties of corn starch. *Carbohydrate Polymers,* **79,** 633-641.

Maruatona, G.N., Duodu, K.G. & Minnaar, A. (2010). Physicochemical, nutritional and functional properties of marama bean flour. *Food Chemistry,* **121,** 400-405.

Méndez-Montealvo, G., García-Suárez, F.J., Paredes-López, O. & Bello-Pérez, L.A. (2008). Effect of nixtamalization on morphological and rheological characteristics of maize starch. *Journal of Cereal Science,* **48,** 420-425.

Milán-Carrillo, J., Gutiérrez-Dorado, R., Cuevas-Rodríguez, E., Garzón-Tiznado, J. & Reyes-Moreno, C. (2004). Nixtamalized flour from quality protein maize (*Zea mays* L.). Optimization of alkaline processing. *Plant Foods for Human Nutrition,* **59,** 35-44.

Milán-Carrillo, J., Gutiérrez-Dorado, R., Perales-Sánchez, J.X.K., Cuevas-Rodríguez, E.O., Ramírez-Wong, B. & Reyes-Moreno, C. (2006). The optimization of the extrusion process when using maize flour with a modified amino acid profile for making tortillas. *International Journal of Food Science and Technology,* **41,** 727-736.

Mora-Rochin, S., Gutiérrez-Uribe, J.A., Serna-Saldivar, S.O., Sánchez-Peña, P., Reyes-Moreno, C. & Milán-Carrillo, J. (2010). Phenolic content and antioxidant activity of tortillas produced from pigmented maize processed by conventional nixtamalization or extrusion cooking. *Journal of Cereal Science,* **52,** 502-508.

Murthy, K.V., Ravi, R., Bhat, K.K. & Raghavarao, K. (2008). Studies on roasting of wheat using fluidized bed roaster. *Journal of Food Engineering,* **89,** 336-342.

Nyembwe, P., Minnaar, A., Duodu, K.G. & De Kock, H.L. (2015). Sensory and physicochemical analyses of roasted marama beans [*Tylosema esculentum* (Burchell) A. Schreiber] with specific focus on compounds that may contribute to bitterness. *Food Chemistry,* **178,** 45-51.

Oboh, G. (2005). Effect of blanching on the antioxidant properties of some tropical green leafy vegetables. *LWT - Food Science and Technology,* **38,** 513-517.

Oboh, G., Ademiluyi, A.O. & Akindahunsi, A.A. (2010). The effect of roasting on the nutritional and antioxidant properties of yellow and white maize varieties. *International Journal of Food Science and Technology,* **45,** 1236-1242.

Oikonomou, N. & Krokida, M. (2011). Literature data compilation of wai and wsi of extrudate food products. *International Journal of Food Properties,* **14,** 199-240.

Ollett, A.L., Parker, R., Smith, A.C., Miles, M.J. & Morris, V.J. (1990). Microstructural changes during the twin-screw extrusion cooking of maize grits. *Carbohydrate Polymers,* **13,** 69-84.

Pappa, M.R., De Palomo, P.P. & Bressani, R. (2010). Effect of lime and wood ash on the nixtamalization of maize and tortilla chemical and nutritional characteristics. *Plant Foods for Human Nutrition,* **65,** 130-135.

Park, M., Kim, K. & Kim, J. (1993). Changes in the physicochemical properties of ginseng by roasting. *Journal of Ginseng Research,* **17,** 228-231.

Pittia, P., Dalla Rosa, M. & Lerici, C. (2001). Textural changes of coffee beans as affected by roasting conditions. *LWT-Food Science and Technology,* **34,** 168-175.

Pollack, A. (2011). Us approves corn modified for ethanol. *The New York Times, February 2011.*

Pomeranz, Y., Martin, C., Traylor, D. & Lai, F. (1984). Corn hardness determination. *Cereal Chemistry,* **61,** 147-150.

Pratt, R., Paulis, J., Miller, K., Nelsen, T. & Bietz, J. (1995). Association of zein classes with maize kernel hardness. *Cereal Chemistry,* **72,** 162-166.

Quintanar Guzmán, A., Jaramillo Flores, M.E., Mora Escobedo, R., Chel Guerrero, L. & Solorza Feria, J. (2009). Changes on the structure, consistency, physicochemical and viscoelastic properties of corn (*Zea mays* sp.) under different nixtamalization conditions. *Carbohydrate Polymers,* **78,** 908-916.

Ranum, P., Peña-Rosas, J.P. & Garcia-Casal, M.N. (2014). Global maize production, utilization, and consumption. *Annals of the New York Academy of Sciences,* **1312,** 105-112.

Ratnayake, W.S. & Jackson, D.S. (2006). Gelatinization and solubility of corn starch during heating in excess water: New insights. *Journal of Agricultural and Food Chemistry,* **54,** 3712-3716.

Riaz, M.N., Asif, M. & Ali, R. (2009). Stability of vitamins during extrusion. *Critical Reviews in Food Science and Nutrition,* **49,** 361-368.

Rice-Evans, C., Miller, N. & Paganga, G. (1997). Antioxidant properties of phenolic compounds. *Trends in Plant Science,* **2,** 152-159.

Ruiz-Gutiérrez, M.G., Quintero-Ramos, A., Meléndez-Pizarro, C.O., Lardizábal-Gutiérrez, D., Barnard, J., Márquez-Melendez, R. & Talamás-Abbud, R. (2010). Changes in mass transfer, thermal and physicochemical properties during nixtamalization of corn with and without agitation at different temperatures. *Journal of Food Engineering,* **98,** 76-83.

Saklar, S., Ungan, S. & Katnas, S. (2003). Microstructural changes in hazelnuts during roasting. *Food Research International,* **36,** 19-23.

Salazar, R., Arámbula-Villa, G., Luna-Bárcenas, G., Figueroa-Cárdenas, J.D., Azuara, E. & Vázquez-Landaverde, P.A. (2014). Effect of added calcium hydroxide during corn nixtamalization on acrylamide content in tortilla chips. *LWT - Food Science and Technology,* **56,** 87-92.

Sánchez-Madrigal, M., Quintero-Ramos, A., Martínez-Bustos, F., Meléndez-Pizarro, C., Ruiz-Gutiérrez, M., Camacho-Dávila, A., Torres-Chávez, P. & Ramírez-Wong, B. (2014). Effect of different calcium sources on the bioactive compounds stability of extruded and nixtamalized blue maize flours. *Journal of Food Science and Technology,* **52**, 2701-2710.

Santillán-Moreno, A., Martínez-Bustos, F., Castaño-Tostado, E. & Amaya-Llano, S.L. (2011). Physicochemical characterization of extruded blends of corn starch–whey protein concentrate–agave tequilana fiber. *Food and Bioprocess Technology,* **4,** 797-808.

Sefa-Dedeh, S., Cornelius, B., Sakyi-Dawson, E. & Afoakwa, E.O. (2004). Effect of nixtamalization on the chemical and functional properties of maize. *Food Chemistry,* **86,** 317-324.

Sharma, P., Gujral, H.S. & Singh, B. (2012). Antioxidant activity of barley as affected by extrusion cooking. *Food Chemistry,* **131,** 1406-1413.

Singh, S., Gamlath, S. & Wakeling, L. (2007). Nutritional aspects of food extrusion: A review. *International Journal of Food Science and Technology,* **42,** 916-929.

Srivastav, P., Das, H. & Prasad, S. (1990). Effect of roasting process variables on in-vitro protein digestibility of bengalgram, maize and soybean. *Food Chemistry,* **35,** 31-37.

Summa, C., Raposo, F.C., Mccourt, J., Scalzo, R.L., Wagner, K.-H., Elmadfa, I. & Anklam, E. (2006). Effect of roasting on the radical scavenging activity of cocoa beans. *European Food Research and Technology,* **222,** 368-375.

USDA (2015a). Corn production by country in 1000MT. United States Department of Agriculture. URL: www.indexmundi.com/agriculture/?commodity=corn Accessed 21/February/2015.

USDA (2015b). USDA national nutrient database for standard reference release 27. United States Department of Agriculture. URL: http://ndb.nal.usda.gov/ndb/foods/show/6549?fgcd=&manu=&lfacet=&format=&count=&max=35&offset=&sort=&qlookup=corn Accessed 01/June/2015.

Valderrama-Bravo, C., Rojas-Molina, A., Gutiérrez-Cortez, E., Rojas-Molina, I., Oaxaca-Luna, A., De La Rosa-Rincón, E. & Rodríguez-García, M.E. (2010). Mechanism of calcium uptake in corn kernels during the traditional nixtamalization process: Diffusion, accumulation and percolation. *Journal of Food Engineering,* **98,** 126-132.

Valko, M., Rhodes, C.J., Moncol, J., Izakovic, M. & Mazur, M. (2006). Free radicals, metals and antioxidants in oxidative stress-induced cancer. *Chemico-Biological Interactions,* **160,** 1-40.

Vivas-Rodriguez, N.E., Serna-Saldivar, S.O., Waniska, R.D. & Rooney, L.W. (1990). Effect of tortilla chip preparation on the protein fractions of quality protein maize, regular maize and sorghum. *Journal of Cereal Science,* **12,** 289-296.

Vivek, B. (2008). *Breeding quality protein maize (QPM): Protocols for developing qpm cultivars.* Pp. 1-60. Mexico: CIMMYT.

Waigh, T.A., Gidley, M.J., Komanshek, B.U. & Donald, A.M. (2000). The phase transformations in starch during gelatinisation: A liquid crystalline approach. *Carbohydrate Research,* **328,** 165-176.

Wall, J.S., Cooker, L.A. & Bietz, J.A. (1988). Structure and origin of maize endosperm alcohol-insoluble glutelin. *Journal of Agricultural and Food Chemistry,* **36,** 722-728.

Wang, Y.-Y. & Ryu, G.-H. (2013a). Physical properties of extruded corn grits with corn fibre by CO_2 injection extrusion. *Journal of Food Engineering,* **116,** 14-20.

Wang, Y.-Y. & Ryu, G.-H. (2013b). Physicochemical and antioxidant properties of extruded corn grits with corn fiber by co 2 injection extrusion process. *Journal of Cereal Science,* **58,** 110-116.

Wolf, B. (2010). Polysaccharide functionality through extrusion processing. *Current Opinion in Colloid and Interface Science,* **15,** 50-54.

Wong, S.S., Li, R.H. & Stadlin, A. (1999). Oxidative stress induced by MPTP and MPP[+]: Selective vulnerability of cultured mouse astrocytes. *Brain Research,* **836,** 237-244.

Youn, K.-S. & Chung, H.-S. (2012). Optimization of the roasting temperature and time for preparation of coffee-like maize beverage using the response surface methodology. *LWT - Food Science and Technology,* **46,** 305-310.

Zhu, L.-J., Shukri, R., De Mesa-Stonestreet, N.J., Alavi, S., Dogan, H. & Shi, Y.-C. (2010). Mechanical and microstructural properties of soy protein–high amylose corn starch extrudates in relation to physiochemical changes of starch during extrusion. *Journal of Food Engineering,* **100,** 232-238.
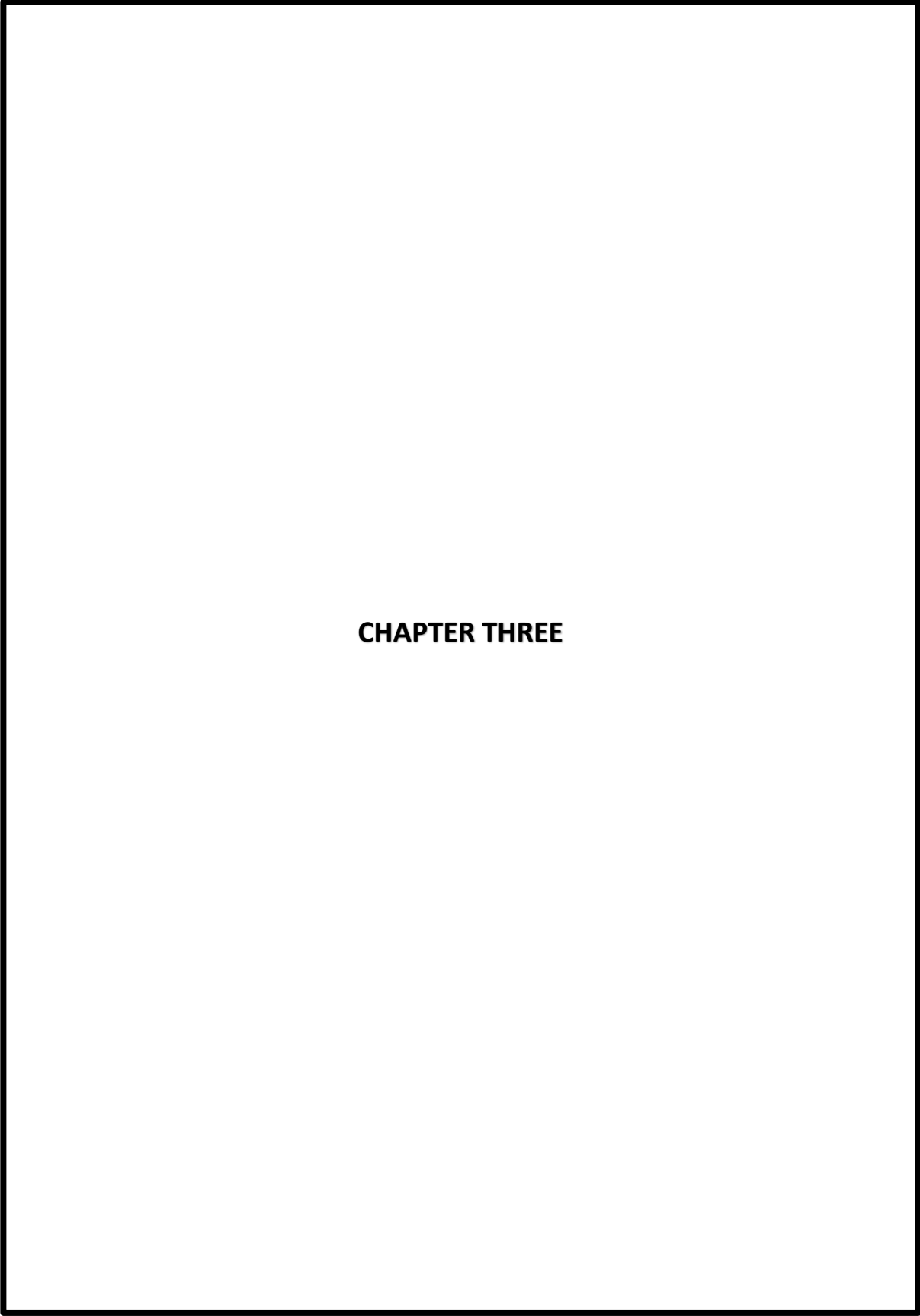
CHAPTER THREE

Chapter 3

Effect of forced convection roasting on physicochemical and antioxidant properties and optimisation of roasting conditions of Nigerian maize (*Zea mays* L.) cultivars for the production of whole grain flour

Abstract

Whole grain maize flour contains dietary fiber, phytochemicals, vitamins, minerals and saturated oil with nutritional importance. The effect of forced convection roasting (FCR) on physicochemical and antioxidant properties of two Nigerian (S28, S33) maize cultivars were investigated and roasting conditions (roasting temperature and rotating speed) optimised. There was a significant (p ≤0.05) decrease in bulk density of each cultivar with increase in temperature and decrease in speed. Increase in temperature significantly increased whiteness index (WI) of S28 (yellow maize) and decreased that of S33 (white maize) while speed (determining roasting time) did not significantly (p >0.05) alter the WI of both cultivars. Significant decrease in yellowness index (YI) of S28 and increase in that of S33 with increase in temperature were observed, whereas changes in YI of both cultivars due to variation in speed were not significant. Variation in temperature and speed did not show significant changes in pH, kernel hardness, protein, amino acids profile, total phenolics, flavonoids and antioxidant activity of both cultivars. Desirability profiles of predicted values showed that the mean optimum roasting conditions were 189.9 °C/90 Hz for S28, and 140.9 °C/49.8 Hz for S33. Amino acids profile and antioxidant properties of the maize studied were not negatively affected by FCR. Whole grain maize flour with the best nutritional quality could be produced using the mean optimum roasting conditions obtained.

Introduction

Maize (*Zea mays* L.) is the most widely cultivated grain crop in the world with a total production of about 990 million metric tons (MMT) and Nigeria was the 13th largest maize producer in 2014 with a total production of 7.5 MMT (USDA, 2015). In developed countries most of the maize cultivated is used for the production of animal feed and raw materials for food, pharmaceutical and non-food industries. Whereas, in developing countries most of the maize produced is used for human consumption. 'Tuwo' is one of the major maize-based foods consumed in Nigeria and other West African countries. It is a gel-like food product normally produced from non-fermented maize flour and hot water (Bolade *et al.*, 2009) and eaten with different types of vegetable soup. The maize flour consumed is usually refined (bran and germ removed) and not pregelatinised. Heat-processing in the presence of water causes swelling, water absorption, loss of crystalline structure of starch leading to amylose leach during an irreversible process of gelatinisation (Jenkins & Donald, 1998).

The choice of heat-processing method depends on ingredients, environment, economy and traditions of people across the world. Researchers have reported on different methods of heat-processing of maize into preprocessed and finished food products such as production of maize tortilla chips by baking (Kayacier & Singh, 2003), nixtamalisation for the preparation of nixtamal, tortilla chips and corn masa (López-Martínez *et al.*, 2012), production of instant flour from quality protein maize (Reyes-Moreno *et al.*, 2003) and corn-lentil extrudates (Lazou & Krokida, 2010) by extrusion, production of maize-bambara groundnut complementary foods (Uvere *et al.*, 2010) and maize beverage (Chung *et al.*, 2011) by roasting. Roasting is a heat-processing method that involves the use of dry heat (Oliviero *et al.*, 2008) resulting in various physicochemical, nutritional and phytochemical changes which can be desirable or undesirable. Desirable changes include enhancing the content and activity of antioxidants (Chung *et al.*, 2011; Jaramillo-Flores *et al.*, 2003), increasing flavour of end-products (Lee & Lee, 2009), improving product quality and shelf life (Cämmerer & Kroh, 2009) and safety (Yazdanpanah *et al.*, 2005). The undesirable decrease in nutritive values are associated with loss of essential amino acids through non-enzymatic browning reactions and loss of vitamins (Özdemir *et al.*, 2001). Reduction in crude protein, dietary fiber, phenolics and flavonoids content of roasted maize grains was reported (Oboh *et al.*, 2010). Roasting has been utilised traditionally in Korea in processing maize for the preparation of maize beverages and ingredients for the production of different types of food (Chung *et al.*, 2011).

Forced convection roasting (FCR) is a novel grain processing technique that has the additional option of using superheated steam (dry steam) to replace the conventional dry heat during roasting process. The superheated steam is forced through the grains while continuously being mixed and moving through the roasting chamber of a forced convection continuous tumble roaster (FCCTR) (Fritz, 2013). The superheated steam and continuous tumbling of the roasting chamber result in even and faster heat transfer into the grains ensuring uniform roasting. There was an increase in water absorption capacity and *in vitro* protein digestibility of marama bean (*Tylosema esculentum*)

dry-heated (roasted) using FCCTR at 150 °C for 20 min and the flour was used in combination with that of sorghum for the production of a composite poridge (Maruatona *et al.*, 2010; Kayitesi *et al.*, 2010; Kayitesi *et al.*, 2012). Nyembwe *et al.* (2015) reported increase in total phenolics of marama beans roasted at 150 °C from 20 to 25 min, but no further increase observed when the time of roasting was increased to 30 min. The shelf life of hazelnut roasted in a forced convection oven under moist and dry heat conditions was determined and compared to that roasted using a ficonventional hot-air drum roaster (Alamprese *et al.*, 2009). Hazelnuts roasted under moist heat conditions showed longer shelf life which was attributed to less destruction of tocopherols and reduction in lipid peroxidation. There has been no published study on FCR of maize or any grain using superheated steam to date.

Response surface methodology (RSM) is often used for studying the effects of, and relationship between, experimental factors and response variables (Kahyaoglu, 2008). It can also be used in empirical building of models for the optimisation of process and/or response variables using a second-degree polynomial equation. RSM saves experimental materials and time by providing useful and reliable information with the lowest possible number of experiments. RSM has been applied successfully in complex food processing optimisation procedures using central composite design (CCD) (Mendes *et al.*, 2001; Reyes-Moreno *et al.*, 2003; Milán-Carrillo *et al.*, 2004; Kahyaoglu, 2008; Uysal *et al.*, 2009; Youn & Chung, 2012). The aim of this study was to investigate the effect of FCR on physicochemical and antioxidant properties of maize cultivars from Nigeria and to optimise the roasting conditions (roasting temperature and rotating speed) for the production of whole grain maize flour using RSM.

Materials and Methods

Materials

Approximately 5 kg each of a yellow [SAMMAZ28 (S28)] and a white [SAMMAZ33 (S33)] registered maize cultivars was obtained from the Institute for Agricultural Research, Samaru (Ahmadu Bello University, Zaria, Nigeria). The S28 (8.10% moisture) and S33 (8.68% moisture) are soft maize grains, widely cultivated and consumed in Northern Nigeria. The uninfected maize samples of uniform kernels size were cleaned by removing foreign materials and broken kernels. Each sample was thoroughly mixed and kept in an airtight plastic container at room temperature prior to use.

Chemicals

Acetone, methanol, ethyl acetate, sodium carbonate (Na_2CO_3), sodium nitrite ($NaNO_2$), aluminium chloride ($AlCl_3$), sodium hydroxide (NaOH), sodium acetate trihydrate ($C_2H_3NaO_2 \cdot 3H_2O$), glacial acetate ($C_2H_4O_2$) and hydrochloric acid (HCl); Folin-Ciocalteau and DPPH (2,2-diphenyl-1-picrylhydrazyl) reagents and gallic acid, ascorbic acid and Catechin standards were purchased from Sigma-Aldrich (St. Louis, USA). An AccQ-Tag Ultra Derivatization Kit was purchased from

Waters Corporation (Massachusetts, USA). Alfalfa standard was purchased from Leco Corporation (Leco Africa, Kempton Park, South Africa).

Tempering of maize kernels

Tempering, to increase the moisture content of the maize kernels to between 18 and 20% as required for the FCCTR, was done according to the American Association of Cereal Chemists International (AACCI) Approved Method 26-95.01 (AACC, 1999). The calculated quantity of water (Eq. 1) was added to the maize samples (200 g/run) in screw capped plastic containers and kept for 72 h at room temperature with shaking at intervals (6 h) to ensure even absorption of moisture by the maize kernels.

$$\text{Water to add (mL)} = \left[\frac{100 - \text{initial moisture (\%)}}{100 - \text{required moisture (\%)}} - 1 \right] \times \text{sample weight (g)} \tag{1}$$

Experimental design

Ten combinations (experimental runs) of roasting temperature (X_1) and rotating speed (X_2) were randomly generated using a CCD consisting of a two-level factorial design (minimum and maximum), two center points (C) and two axial/extreme points (minimum* and maximum*) based on roasting temperature (150 and 220 °C) and rotating speed (determining roasting time) (30 and 90 Hz) limits obtained from earlier preliminary roasting experiments (Fig. 3.1). The response variables (Y) considered were moisture content, bulk density, colour [whiteness index (WI) and yellowness index (YI)], pH, kernel hardness [coarse/fine (C/F) ratio], protein content, amino acids profile [total amino acids (TAA) and total essential amino acids (TEAA)], total phenolics, total flavonoids and DPPH antioxidant activity. Prediction models of the response variables were obtained using the second-degree polynomial equation (Eq. 2).

$$Y = \beta_O + \beta_1 X_1 + \beta_2 X_2 + \beta_{12} X_1 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 \tag{2}$$

where *β~o~* is constant (intercept), *β₁* and *β₂* are linear coefficients, *β₁₁* and *β₂₂* are quadratic coefficients and *β₁₂* is the coefficient of interaction.

Forced convection roasting

Clean tempered maize kernels (200 g/run) were roasted in a FCCTR, model R100E (Roastech, Bloemfontein, South Africa) according to the generated experimental runs. The FCCTR was operated at 150 °C/20 Hz and 2 kg of tempered maize (different cultivar) grains roasted to generate superheated steam which replaced the hot dry-air in the roasting chamber prior to the roasting of the 200 g/run samples. The 200 g/run roasted samples were cooled to room temperature and milled using a Cyclone Laboratory Mill, model 3100 (Perten Instruments, Hagersten, Sweden) fitted with 0.8 mm sieve. The flour obtained were stored in screw capped plastic containers at 4 °C before analyses.
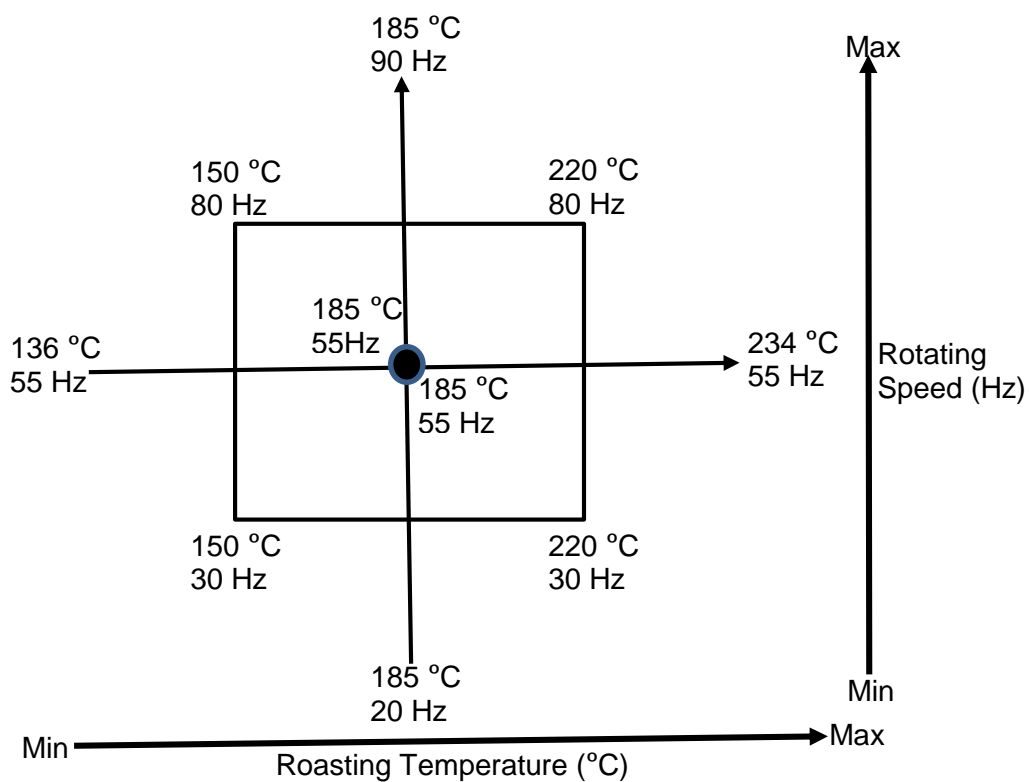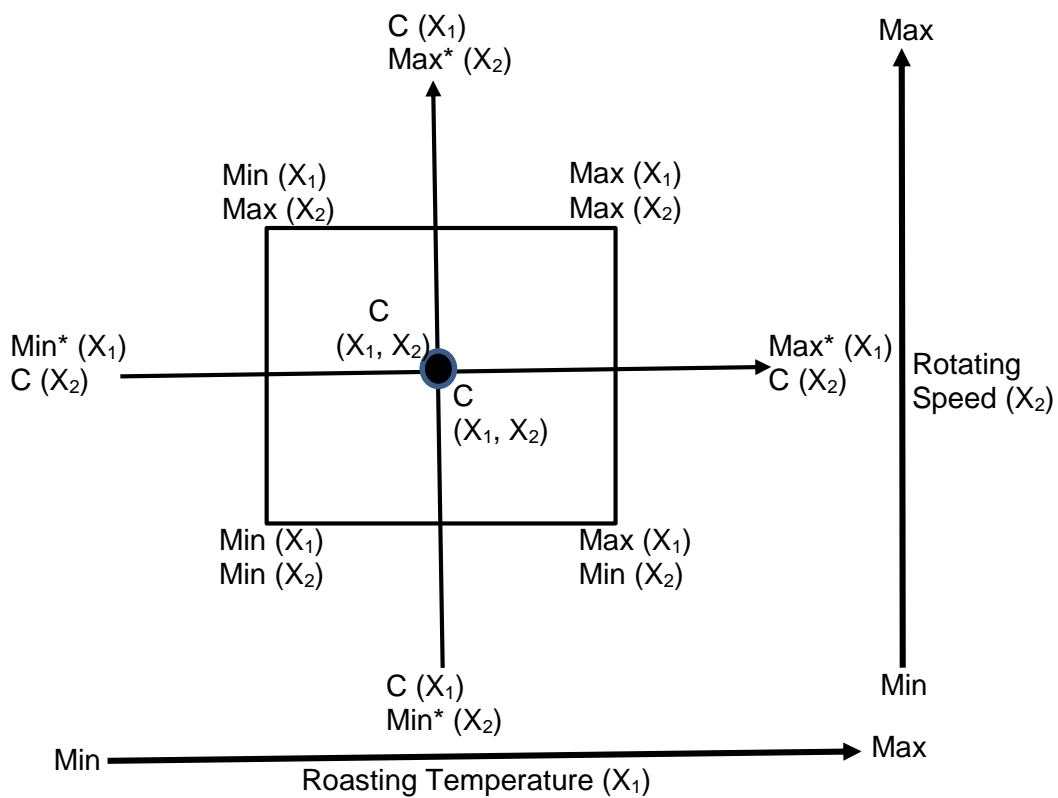
Figure 3.1. Ten experimental runs (roasting temperature and rotating speed combinations) generated using a central composite design.

Determination of moisture content

Moisture content was determined as described in AACCI Approved Method 44–19.01 (AACC, 1999). Maize flour (2 ± 0.001 g) was heated in an aluminium moisture dish for 2 h at 135 °C in an Oven, model EM10 (CHOPIN Technologies, Cedex, France). Moisture content was determined in triplicate. Percentage moisture was calculated using equation 3.

$$\text{Moisture (\%)} = \frac{\text{loss in moisture} \times 100}{\text{weight of sample}} \tag{3}$$

Determination of bulk density

Bulk density was determined as explained by Chung *et al*. (2011). Maize kernels were weighed in a container of known volume using a Compact Laboratory Balance, model ATA620 (Axis Sp, Gdansk, Poland) and expressed as weight-to-volume ratio (Eq. 4). Triplicate determinations were performed.

$$\text{Bulk density (g/cm}^3) = \frac{\text{weight}}{\text{volume}} \tag{4}$$

Determination of colour

Colour of the roasted maize flour was measured in triplicate as CIELAB coordinates (*L**, *a**, *b**) using the Color-guide gloss 45/0 spectrophotometer (BYK-Gardner, Geretsried, Germany) after calibration with a light green standard tile of known coordinates. Numerical values of the coordinates were recorded as *L** (from 0 = black to +100 = white), *a** (from + value = red to – value = green) and *b** (from + value = yellow to – value = green) (Ayala-Rodríguez *et al.*, 2009). The WI and YI where estimated using equations 5 and 6 (Pathare *et al.*, 2013).

$$\text{WI} = 100 - [(100 - L*)^2 + a*^2 + b*^2]^{0.5} \tag{5}$$

$$\text{YI} = \frac{142.86 \, b*}{L*} \tag{6}$$

Determination of pH

The pH of the roasted maize flour was determined in triplicate according to AACCI Approved Method 02–52.01 (AACC, 1999) with minor modifications. About 10 g of the flour was weighed into a glass vial, 100 mL distilled water added and sonicated in a 40 KHz Ultrasonic Water Bath, model DC400H (MRC Ltd, Tel-Aviv, Israel) for 20 min. The mixture was allowed to stand for 10 min and the supernatant carefully decanted. The pH was immediately determined while stirring at room temperature using a pH meter (Crison, Barcelona, Spain) already calibrated with three known buffer solutions (pH 4, 7 and 9.2).

Determination of kernel hardness

Maize kernel hardness was determined in duplicate by means of the particle size index (PSI) method, using milling and sieving protocols as described by O'Kennedy.(2011). Maize kernels (50 g) was milled using a Cyclone Laboratory Mill, model 3100 fitted with a 1 mm sieve. Ten grams of maize flour were weighed onto the 150 µm sieve and 10 g of whole wheat was put onto each of the 150 and 75 µm sieves. Two sets of sieves and pans were stacked together on a Retsch Tap Sieve Shaker, model AS200 (Retsch, Haan, Germany) for 10 min. The whole wheat kernels were added to obtain effective sieving of the flour. After sieving, fine maize flour adhering to the bottom of the 150 µm sieve were brushed gently into the 75 µm sieve and fine flour adhering to the bottom of the 75 µm were brushed gently into the receiving pan. Three fractions (PSI_1, PSI_2 and PSI_3) were calculated using equations 7, 8 and 9.

$$PSI_1 = \frac{W_1 - (W_{150\mu m\ sieve} + W_{wheat\ in\ 150\mu m\ sieve})}{W_{maize\ flour}} \tag{7}$$

$$PSI_2 = \frac{W_2 - (W_{75\mu m\ sieve} + W_{wheat\ in\ 75\mu m\ sieve})}{W_{maize\ flour}} \tag{8}$$

$$PSI_3 = \frac{(W_3 - W_{pan})}{W_{maize\ flour}} \tag{9}$$

where W_1 = weight of 150 µm sieve and its content after sieving, W_2 = weight of 75 µm sieve and its content after sieving, W_3 = receiving pan and its content after sieving, $W_{150\mu m\ sieve}$ = weight of empty 150 µm sieve, $W_{75\mu m\ sieve}$ = weight of empty 75 µm sieve, $W_{wheat\ in\ 150\mu m\ sieve}$ = weight of wheat kernels in 150 µm sieve, $W_{wheat\ in\ 75\mu m\ sieve}$ = weight of wheat kernels in 75 µm sieve, W_{pan} = weight of empty pan, $W_{maize\ flour}$ = weight of maize flour. The ratio of larger particles (PSI_1) to smaller particles ($PSI_2 + PSI_3$) was calculated as coarse/fine (C/F) ratio (Eq. 10). Higher value of C/F ratio indicates harder maize kernels while lower value indicates softer maize kernel.

$$C/F = \frac{PSI_1}{(PSI_2 + PSI_3)} \tag{10}$$

Determination of crude protein

Crude protein content of the roasted maize flour was determined in duplicate by the Dumas combustion method as described in AACCI Approved Method 46–30.01 (AACC, 1999) using a Leco, model FP-528 (Leco Africa, Kempton Park, South Africa). Calibration was done with an Alfalfa standard which has a known nitrogen content of 3.38 ± 0.04%. Alfalfa (0.1 g) was analysed after running blank (empty) analysis in order to confirm the accuracy of the instrument before the determination of nitrogen in the flour. About 0.5 g of sample was used for the combustion. Each sample was weighed onto a tin foil cup, twisted, rolled into an egg shape and loaded into the instrument. The combustion temperature used was 850 °C for pyrolysis of sample in pure (99.9%)

oxygen. Recorded nitrogen content was converted to protein by multiplying with the conversion factor 5.68 (Sriperm *et al.*, 2011) and expressed on a 12% moisture basis (Eq. 11).

$$APC\ (\%) = MPC * \frac{100 - FMC}{100 - OMC} \tag{11}$$

where: APC = adjusted protein content, MPC = measured protein content, FMC = final moisture content (12%) and OMC = original moisture content of sample.

Determination of amino acids profile

Roasted maize flour (100 mg) was hydrolysed with 6 mL of 6 N 15% phenolic HCl at 110 °C overnight. Amino acids in the hydrolysates were determined in duplicate using liquid chromatography mass spectrometry (LC-MS) (CAF, 2014). The LC was performed in a Waters API Quattro Micro UPLC (Waters Corporation, Massachusetts, USA) using Waters AccQ-Tag Ultra Derivatization Kit (Waters Corporation, Massachusetts, USA). For sample preparation, 10 µL of undiluted hydrolysates was added to the Waters AccQ-Tag Kit constituents and heated at a temperature of 55 °C for 10 min in a heating block. The column used was AccQ-Tag C18 (1.7 µm, 2.1 x 100 mm) and a flow rate of 0.7 mL/min was considered for the gradient elution. The column temperature was maintained at 36 °C and the detection source was ESI$^+$ (Electrospray ionisation). Injection was done using Modify ACQUITY Binary Solvent Manager (Waters Corporation, Massachusetts, USA) and the injection volume was 1 µL.

The two solvents used were Eluent A2 [100 mL eluent A concentrate (6-aminoquinolyl-N-hydroxysuccinimidyl carbamate in acetonitrile) and 900 mL distilled water] and Eluent B (acetonitrile). The MS analysis was done using Waters ACQUITY Tandem Triple Quadrupole spectrometer (Waters Corporation, Massachusetts, USA). The MS conditions were set at 3.5 kV for capillary voltage, 15 V for cone voltage and source and desolvation temperatures of 120 and 350 °C, respectively. Desolvation and cone gases were set at 350 and 50 L/h, respectively. Out of the twenty naturally occurring amino acids in protein tryptophan, glutamine and asparagine were not determined. The total essential amino acids (TEAA) comprised of arginine, histidine, valine, threonine, isoleucine, leucine, lysine, phenylalanine and methionine while total amino acids (TAA) consisted of TEAA, serine, glycine, aspartate, glutamate, alanine, proline, cysteine and tyrosine.

Extraction of phenolic compounds

Free and bound phenolic compounds were extracted using the methods of Wang *et al.* (2013) with minor modification. For free phenolic compounds, the roasted maize flour (1 g) was weighed into a glass vial, 15 mL of 60% chilled aqueous acetone added and sonicated for 10 min at 20 °C in a 40 KHz ultrasonic water bath. The mixture was centrifuged in an Eppendorf Centrifuge, model 5810R (Eppendorf AG, Hamburg, Germany) for 10 min at 2500 g and 4 °C, supernatant collected and the residue re-centrifuged twice with 15 mL chilled aqueous acetone. The supernatants were pooled

together and evaporated to dryness. The extract was reconstituted in 5 mL 70% aqueous methanol. For bound phenolic compounds, the residue above was digested with 10 mL of 2 M NaOH for 1 h at room temperature. The digest was neutralised with 6 M HCl to a pH between 1.45 and 1.55 and extracted with 15 mL absolute ethyl acetate 4 times by centrifuging for 10 min at 2500 g and 4 °C. The ethyl acetate extracts were pooled together, evaporated to dryness and reconstituted in 5 mL of 70% aqueous methanol. The free and bound phenolic compounds reconstituted extracts were pooled together, filtered and stored at -80 °C prior to analyses.

Determination of total phenolics content

Total phenolics content was determined in triplicate using Folin-Ciocalteau method as described by Žilić *et al*. (2012). Standard (gallic acid) and extract (100 µL each) was put into labelled Eppendorf tube and 400 µL of distilled water added. The mixture was neutralised with 1.25 mL of 20% aqueous Na_2CO_3, allowed to stand in the dark for 40 min at room temperature and the absorbance measured using a Helios Omega UV-vis spectrophotometer (Thermo Scientific Technologies, Madison, USA) at 725 nm against an absolute methanol blank. Total phenolics content was expressed as gram of gallic acid equivalent per 100 g of dry matter (g GAE/100 g DM) using a gallic acid standard curve.

Determination of total flavonoids content

Total flavonoids content was determined in triplicate using the method described by Yang *et al*. (2009). Standard (catechin) and extract (250 µL each) was transferred into a centrifuge tube and 1.25 mL of distilled water added. A 5% $NaNO_2$ (75 µL) was added, the mixture shaken and allowed to stand for 5 min in the dark at room temperature. A 10% $AlCl_3$ (150 µL) was added, the mixture shaken and kept in the dark for 6 min. Distilled water (775 µL) was added after adding 500 µL of 1 M NaOH and the absorbance measured at 510 nm. Total flavonoids content was expressed as milligram of catechin equivalent per gram of dry matter (mg CE/g DM) using a catechin standard curve.

Determination of antioxidant activity

DPPH radical scavenging activity was determined according to the method described by Karioti *et al.* (2004). Standard (ascorbic acid) and extract (20 µL each) was put into an Eppendorf tube, 800 µL of absolute methanol added and the mixture shaken. A 0.1 mM DPPH solution (1 mL) was added, the mixture shaken and kept in the dark for 60 min at room temperature. The absorbance was measured at 517 nm. DPPH antioxidant activity was expressed as millimolar ascorbic acid equivalent per gram of dry matter (mM AAE/g DM).

Statistical analysis

Average values of the response variables were subjected to RSM analysis consisting of analysis of variance (ANOVA), partial F-test and regression analysis using Statistica version 12 (StatSoft Inc, Oklahoma, USA). Regression coefficients, standardised effect estimate (effect size) and *p*-values of linear, quadratic and interaction effects for X_1 and X_2 were determined. Significance of effects (linear, quadratic and interaction) of X_1 and X_2 on each of the response variables was expressed as effect size at 95 % confidence interval. Prediction models and their respective fitted response surface plots were determined. Coefficient of determination (R^2) was used to compare variations as a result of differences in experimental treatments with variations due to errors in measurement of the response variables (Bezerra *et al.*, 2008). Determination of optimum roasting conditions was done using desirability profiling.

Results and Discussion

ANOVA and RSM data analyses

Effect size and corresponding *p*-values were used for explanation of statistical significance of the linear, quadratic and interaction effects of X_1, X_2 on the response variables. Significance of these effects were shown for moisture content, WI and YI (used for optimisation of roasting conditions) using standardised Pareto charts. Effect size defines the strength of significance of terms in the regression equation (Eq. 2). The higher the effect size the stronger the level of significance. Positive and negative effects showed positive and negative relationships with the dependent variable, respectively. Regression coefficients, R^2 and *p*- values of lack-of-fit were used to indicate how well the prediction model (regression equation) generated, fits the experimental data. Graphical representation of the prediction models were presented as three-dimensional (3-D) fitted response surface plots which indicated the magnitude of a response variable at given temperature and speed of roasting. For a prediction model to have a good fit with experimental data, its R^2 value should be ≥0.8 and have a non-significant lack-of-fit (Guan & Yao, 2008). Prediction models for moisture content, WI and YI with R^2 >0.80 and non-significant (*p* >0.05) lack-of-fits were selected for the optimisation of roasting conditions using desirability profiling. Prediction model of each response variable was calculated using the regression coefficients (β_o, β_1, β_2, β_{12}, β_{11}, and β_{22}) in the second-degree polynomial equation (Eq. 12). Moisture content of S28 for instance:

$$Y = 9.14503 - 0.03410X_1 + 0.25860X_2 + 0.00015X_1X_2 - 0.00061X_1^2 - 0.00084X_2^2 \qquad (12)$$

where Y = moisture content (%), X_1 = temperature (°C) and X_2 = speed (Hz).

Effect of roasting temperature and rotating speed on the response variables

Moisture content

The moisture content of the roasted S28 and S33 samples ranged from 10.00 to 14.38 and 10.20 to 14.54% (Table 3.1), respectively. R^2 values of 0.82 and 0.90 obtained for S28 and S33 (Table 3.3), respectively with non-significant (p >0.05) lack-of-fit indicated that the prediction models of moisture content for the maize cultivars fitted the experimental data very well. Rotating speed showed significant (p ≤0.05) linear effect on the moisture content of S28 and S33 with positive effect sizes of 2.81 and 4.61 (Fig. 3.3), respectively which showed that decrease in speed (thus longer roasting time) significantly decreased moisture content and the effect was higher in S33. The linear effect of temperature on moisture content of S28 was not significant (p >0.05) while that of S33 was; however, both had negative effect sizes of -2.52 and -3.34 (Fig. 3.3), respectively. This was an indication that speed had greater impact on moisture loss compared to temperature. In preliminary roasting experiments, it was observed that the lower the rotating speed, the longer the time of roasting, the greater the degree of roasting and the less the moisture content of the maize (result not shown). Quadratic effects of temperature and speed as well as linear interaction effect on moisture content were not significant in both cultivars (Fig. 3.3).

Moisture content is very important in predicting the shelf life of food products and is associated with respiration and activity of spoilage microorganisms. Hoseney (1994) reported that fungal growth was found to be eliminated at moisture content of <14%. For maize and its products, the moisture content for storage should be ≤13.5 % (Humpf & Voss, 2004). Therefore, S28 could be roasted at speed between 20 and 50 Hz while for S33, the speed should be between 20 and 40 Hz (Fig. 3.2) at any temperature within the experimental range in order to produce whole grain flour with the desirable moisture content (≤13.5%). Optimisation of roasting conditions using any of the response variables must be done in such a way that this desirable moisture content is strictly considered.

Bulk density

Bulk density ranged from 0.63 to 0.74 and 0.58 to 0.73 g/cm^3 (Table 3.1) with R^2 values of 0.93 and 0.97 for S28 and S33 (Table 3.2), respectively. Linear effects of roasting temperature and rotating speed on bulk density of S28 and S33 were significant (Table 3.2). Linear effect of temperature on bulk density of S28 and S33 had negative effect size of -6.13 and -8.74 (Table 3.2), respectively which indicated decrease in bulk density with increase in temperature. The effect sizes of linear effect of speed were 3.63 and 5.77 for S28 and S33 (Table 3.2), respectively indicating decrease in bulk density with decrease in rotating speed. Quadratic effects of temperature and speed as well as linear interaction effect on bulk density of S28 were not significant while those of S33 were.

Decrease in bulk density was attributed to the combined effects of moisture loss, kernel expansion, development of internal pores, increase in volume and decrease in weight of the maize

kernels due to heating (Pittia *et al.*, 2001; Jha, 2005). Saklar *et al.* (2003) reported decrease in density of roasted hazelnut grains due to cell wall separation, increase in intercellular spaces, aggregation and swollen of protein bodies and disruption of cellular cytoplasmic network. Similarly, a study on the effect of fluidized bed roasting on wheat by Murthy *et al.* (2008) indicated significant reduction in bulk density with increase in temperature. Bulk density is an important physical property of preprocessed cereals for storage, transportation and marketing. The bulk density range for the roasted S28 and S33 obtained in this study was comparable to that of roasted Korean maize (Suwon-19) (0.52 to 0.79 g/cm^3) reported by Chung *et al.* (2011) using an electric rotary roaster.

Colour

The WI of flour of roasted S28 and S33 ranged from 59.96 to 64.98 and 80.75 to 86.27 (Table 3.1), respectively with R^2 values of 0.86 and 0.87 and non-significant lack-of-fit (Table 3.3). Temperature showed significant linear effect on the flour WI of S28 and S33 with effect sizes of 3.49 and -3.28 (Fig. 3.3), respectively. This showed the higher the temperature the whiter the flour of the yellow maize cultivar, S28, while for S33 (white maize) the flour WI decreased with increase in temperature. The linear effect of speed on flour WI was not significant (p >0.05). The quadratic effects of temperature and speed on flour WI of both cultivars were not significant. The interaction effect was also not significant in S28 but significant in S33. Hsu *et al.* (2003) reported that the overall whiteness of food products which indicates the degree of discoloration during drying process is represented by WI. Measurement of WI is done to obtain data that closely correlate with the white colour preference of consumers and it combines lightness and yellow-green colour into a single value (Pathare *et al.*, 2013). The closer the WI values to 100 the whiter the flour and the higher the consumer preference. Increase in WI of the flour of S28 (yellow kernel) is attributed to discoloration of yellow pigment of the kernels due to heating while decrease in that of S33 (white kernel) could be as a result of Maillard reaction (non-enzymatic browning). The WI of S33 was found to be >80 which indicated that S33 could be roasted at any temperature and speed combination between 150 and 220 °C and between 30 and 90 Hz (Fig. 3.2), respectively to produce acceptable white whole grain flour. As expected, for S28 the WI was lower than that of S33 due to colour difference of the maize kernels.

The flour YI of roasted S28 and S33 ranged from 53.04 to 61.84 and 16.04 to 24.38 (Table 3.1), respectively. High R^2 values of 0.86 and 0.88 for the prediction models of flour YI of S28 and S33 (Table 3.3), respectively with non-significant lack-of-fit were observed. Temperature showed significant linear effect on flour YI of S28 and S33 with effect sizes of -3.61 and 3.45, respectively (Fig. 3.3). This indicated decrease in flour YI of S28 and increase in that of S33 with increase in temperature. Decrease in flour YI of S28 results in increased flour WI due to discoloration of yellow pigment which agrees with the report of Hsu *et al.* (2003). In contrast, positive effect size of S33 showed increase in flour YI with increase in roasting temperature which could be attributed to

Maillard reactions. As reported by Das *et al.* (2004) increase in heating or infrared radiation intensity increased the YI of white parboiled rice. Linear effects of temperature and speed as well as quadratic effects of temperature and speed were not significant in both cultivars. Linear interaction effect was not significant on the flour YI of S28 but significant on that of S33. The degree of yellowness of foods and food products could be indicated by YI (Rhim *et al.*, 1999). General product degradation and scorching as a result of light, chemical exposure and heat processing are associated with yellowness, which can be measured by YI as a single value (Pathare *et al.*, 2013). Fitted response surface plots showing the relationship of flour YI with roasting temperature and speed (Fig. 3.2) indicated lower values for S33 and higher for S28. This indicated that the higher the flour WI the lower the YI, and roasting within the experimental range preserved the natural flour whiteness of white maize cultivar and improved that of the yellow cultivar.
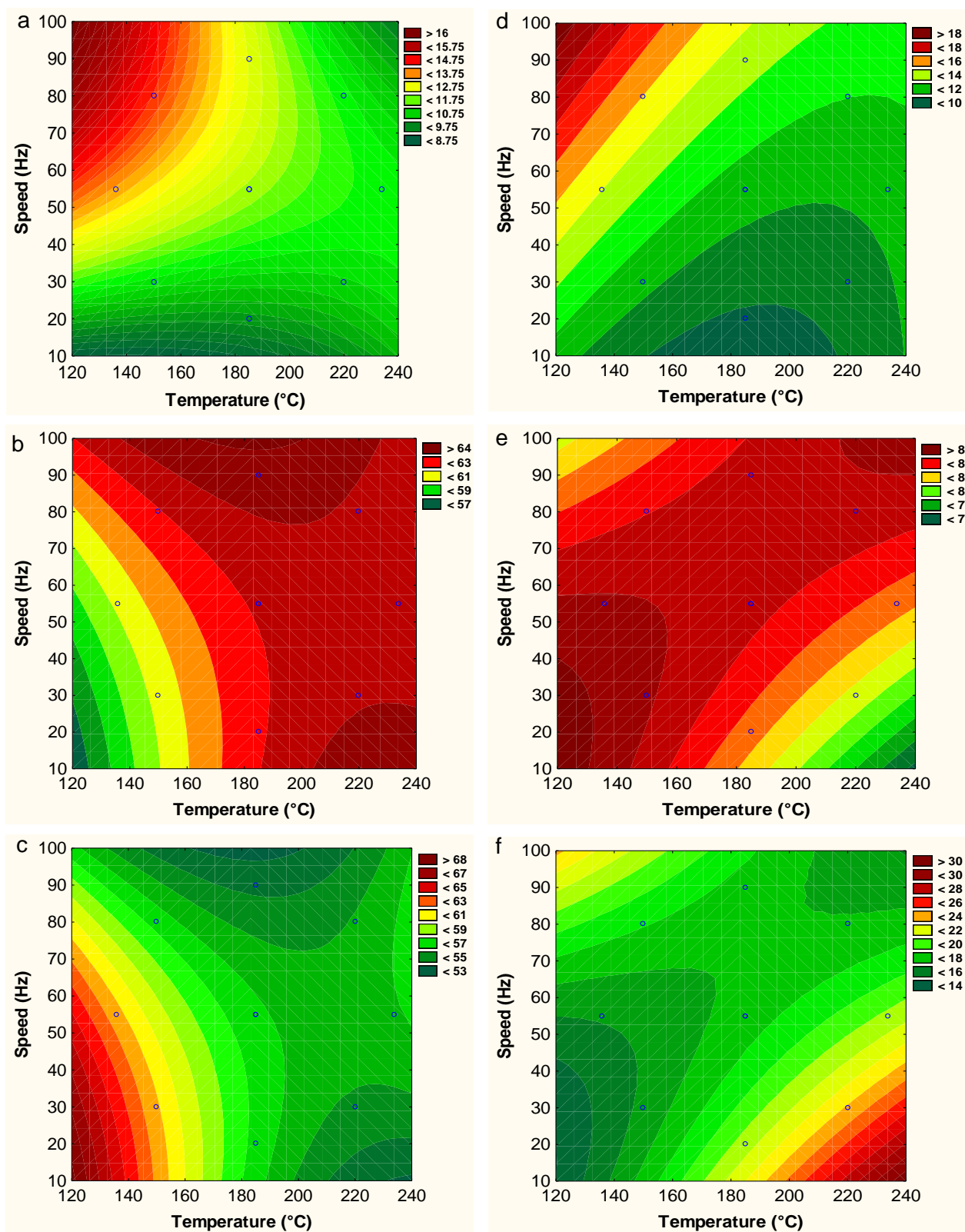
Figure 3.2. Fitted response surface plots (prediction models) of (a) moisture content, (b) whiteness index [WI] and (c) yellowness index [YI] of S28, (d) moisture content, (e) WI and (f) YI of S33 at varying roasting temperatures and rotating speeds.
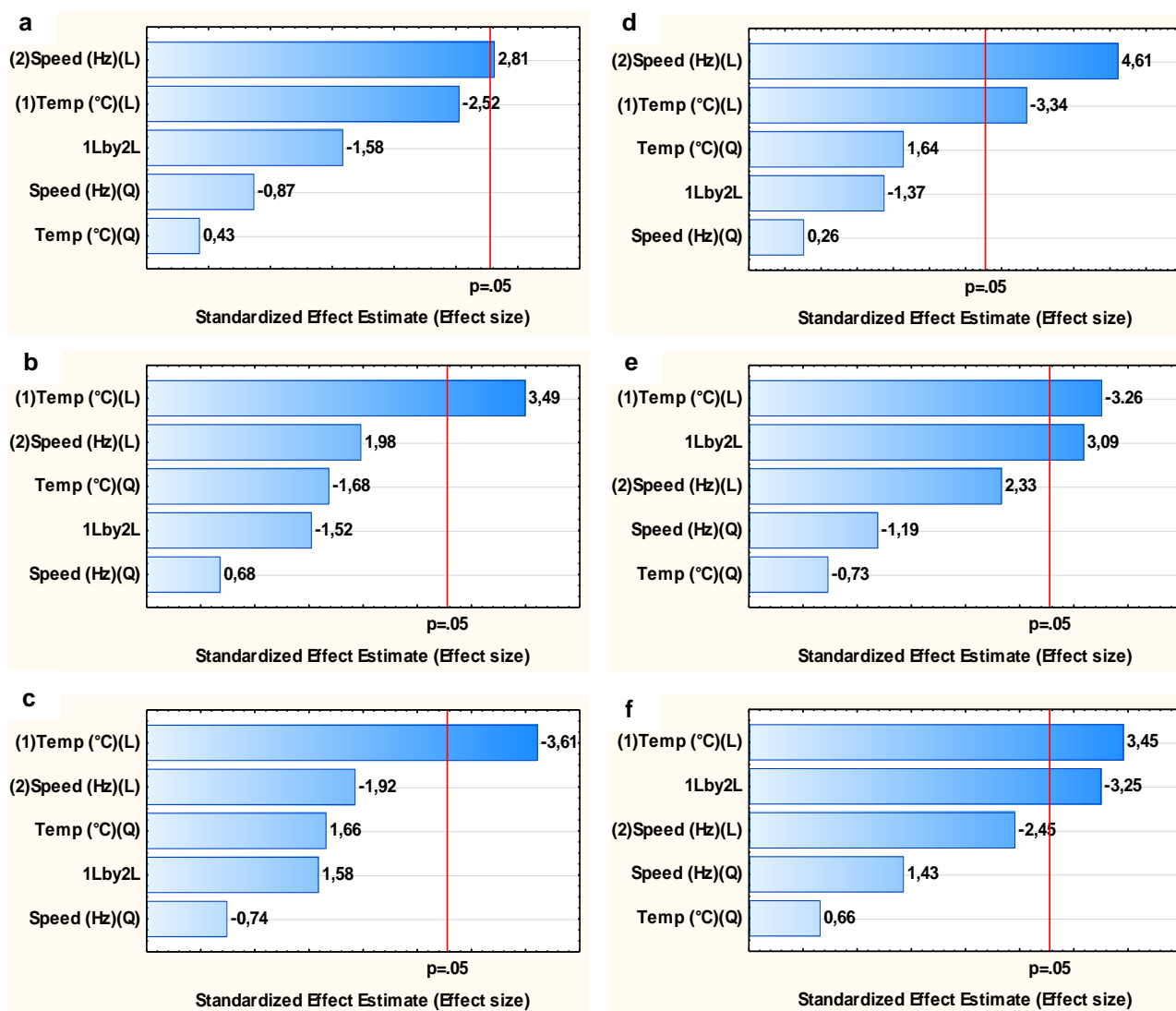
Figure 3.3. Pareto charts of standardised effect estimate (effect size) (p =0.05) of roasting temperature and rotating speed on (a) moisture content, (b) whiteness index [WI] and (c) yellowness index [YI] of S28, and (d) moisture content, (e) WI and (f) YI of S33 (crossing the vertical red line by a bar at p =0.05 indicated significant effect).

pH

The pH value of food substances is the free hydrogen ions (measure of acidity) available, and maize was reported to be a low acid food (pH >4.6) (McGlynn, 2015) with a range of 6.0 to 7.2 (FDA, 2015). Normal heat-processing condition of maize should not significantly lower its pH to below 6.0 which indicates increase in acidity. The pH of the roasted S28 and S33 ranged from 6.09 to 6.28 and 6.05 to 6.23 (Table 3.1) with R^2 values for the prediction models of 0.68 and 0.69 (Table 3.2), respectively. Temperature and speed linear effects, temperature and speed quadratic effects as well as interaction effect on the pH of both cultivars were not significant (Table 3.2). FCR thus did not result in a decrease in pH in contrast to Chung *et al.* (2011) who reported significant decrease in pH of electric rotary roasted Korean maize (Suwon-19) with increase in roasting

temperature (160 to 240 °C) and time (0 to 50 min). Hernandez *et al.* (2007) reported that dry hot-air roasting of Columbian green coffee beans (*Arabica*) at high temperatures (>190 °C) was associated with chemical changes such as hydrolysis, polymerization and oxidation reactions. These chemical reactions were responsible for decreasing the pH of the roasted coffee grains resulting in increased acidity of the products. Similarly, roasting ginseng seeds at high temperature greater than 190 °C caused the conversion of sugars to acidic compounds (Park *et al.*, 1993) which also led to decrease in pH. Therefore, maintaining the pH of roasted maize flour by FCR could be attributed to replacement of dry hot-air with superheated steam during the roasting process. This might be responsible for preventing pyrolytic reactions and conversion of sugars to acidic compounds.

Kernel hardness

Kernel hardness of the roasted S28 and S33, expressed as C/F ratio, was found to be in the range of 2.16 to 2.80 for S28 and 2.17 to 3.17 for S33 (Table 3.1). The R^2 values of 0.76 and 0.41 were obtained for C/F ratio of S28 and S33 (Table 3.2), respectively. Temperature and speed linear effects, temperature and speed quadratic effects as well as interaction effect on C/F ratio of the maize cultivars were not significant. This indicated that roasting the S28 and S33 samples using FCCTR at roasting temperatures and speeds within the experimental range did not significantly alter their kernel hardness. The C/F ratio accurately and objectively provides an indirect but precise estimation of the hard and soft fractions of maize endosperm (Blandino *et al.*, 2010) which defines kernel hardness.

Crude protein

Crude protein content of the roasted S28 and S33 on 12% moisture basis ranged from 8.14 to 8.43 and 8.16 to 8.73% (Table 3.1) with R^2 values of 0.26 and 0.14 (Table 3.2), respectively. Variation in roasting temperature and speed did not show significant (p >0.05) changes in crude protein content of the maize cultivars (Table 3.2). This could perhaps be due to the use of superheated steam for roasting instead of the usual dry hot air. Increase in crude protein concentration of cooked beans and chickpeas was reported by Wang *et al.* (2010) which was due to decrease in soluble solids during cooking. Decrease in soluble solids might have been prevented in the process of roasting the maize using FCCTR. Hefnawy (2011) reported that boiling, autoclaving and microwave cooking of lentils did not show significant changes in total protein content. Similarly, flame roasting of maize at roasting temperatures between 80 and 160 °C had no significant effect on protein content (Costa *et al.*, 1976; McNiven *et al.*, 1994) which agreed with the present finding. Therefore, roasting maize grains using FCCTR within the experimental range would not result in significant change in crude protein content.

Amino acids profile

The amino acids profile indicated that TAA ranged from 4.37 to 5.61 and 4.11 to 5.85, while the TEAA range was from 2.33 to 2.51 and 1.83 to 2.74 for S28 and S33, respectively (Table 3.1). The R^2 values of TAA for S28 and S33 were found to be 0.52 and 0.37 while those of TEAA were 0.43 and 0.35 (Table 3.2), respectively. Temperature and speed linear effects, temperature and speed quadratic effects as well as interaction effect did not show significant changes in TAA and TEAA of both cultivars except the temperature linear effect on TAA of S28 which was significant with positive effect size (14.17). This explained that roasting of S28 and S33 using FCCTR within the experimental range did not significantly alter TAA and TEAA of the maize cultivars, but increase in roasting temperature resulted in significant (p ≤0.05) increase in TAA of S28. Heat treatment causes loss of arginine, lysine, serine and threonine in cotton-seed meal, meat meal and soybean meal (McNaughton & Reece, 1980; Craig & Broderick, 1981; Batterham *et al.*, 1986). Therefore, roasting maize using FCCTR would ensure that the available EAA in the grains is not lost. The increase in crude protein of S28 maize cultivar could be related to the report of Wang *et al.* (2010) which showed increase in protein concentration of cooked beans and chickpeas due to loss of soluble solids due to cooking.

Total phenolics, flavonoids and DPPH antioxidant activity

Roasted S28 and S33 had total phenolics content in the range of 1.42 to 1.73 and 1.08 to 1.46 g GAE/100g (Table 3.1) with R^2 values of 0.59 and 0.75 (Table 3.2), respectively. For total flavonoids, the range was between 0.33 and 0.41 and between 0.15 and 0.29 mg CE/g (Table 3.1) with R^2 values of 0.40 and 0.72 (Table 3.2), respectively. The DPPH antioxidant activity of S28 and S33 ranged from 606.30 to 699.17 and 508.26 to 708.63 mM AAE/g (Table 3.1) with R^2 values of 0.26 and 0.70 (Table 3.2), respectively. There were no significant changes in the linear, quadratic and interaction effects of temperature and speed on total phenolics and flavonoids contents and DPPH antioxidant activity of both cultivars. The results indicated that changes in temperature and speed combinations within the experimental range did not cause significant variation in total phenolics and flavonoids and DPPH antioxidant activity of the maize cultivars.

Decrease or increase in phenolic compounds and antioxidant activity might be different in various types of foods depending on the heat-processing method employed. Sand and microwave oven roasting of barley at 280 ± 5 °C for 20 s decreased total phenolics content by 8.5 to 49.6% and total flavonoids by 24.5 to 53.2%, while the antioxidant activity increased by 16.8 to 108.2% (Sharma & Gujral, 2011). Oven roasting of baru nuts (*Dipteryx alata* Vog) at 150 °C for 45 min did not show significant change in total phenolics content compared to the raw nut, but there was significant decrease in DPPH antioxidant activity (Lemos *et al.*, 2012). Nicoli *et al.* (1999) showed decrease in antioxidant content of roasted coffee, but the antioxidant activity increased. During roasting of apricot kernel and baru nuts, their antioxidant content and activity significantly increased due to the production of new compounds (by Maillard reactions) with phenolic-like

structure (melanoidins).(Durmaz & Alpaslan, 2007; Lemos *et al.*, 2012). Roasting results in chemical degradation and modification of phenolic compounds. It was reported that the modified phenolic compounds such as phenylindans demonstrated high antioxidant capacity (Guillot *et al.*, 1996). Therefore, the ability of FCCTR to prevent significant loss of antioxidant content and activity might be attributed to the use of superheated steam and rotation of grains during the roasting process. This should have reduced the impact of dry heat (responsible for the Maillard reaction) on the maize grains. Most phenolic compounds (phenolic acids and flavonoids) found in cereal grains are concentrated in the bran, therefore consumption of whole grain food products compared to those refined grain was recommended for health benefits (Adom & Liu, 2002). Thus, consumption of whole grain maize flour of the roasted maize cultivars would be of immense health benefits due to the presence of bran and germ.

Table 3.1. Roasting temperatures, rotating speeds of experimental runs generated using a central composite design and average values of the response variables of roasted S28 and S33 maize cultivars

Experimental run	Moisture (%)	BD (g/cm³)	WI flour	YI flour	pH	C/F ratio	Protein (%)	TAA (g/100g)	TEAA (g/100g)	TP (g GAE/100g)	TF (mg CE/g)	DPPH (mM AAE/g)
S28												
136°C/55Hz	13.93	0.73	59.96	61.84	6.28	2.78	7.55	4.37	2.40	1.67	0.35	606.30
150°C/30Hz	10.00	0.72	60.40	61.05	6.11	2.44	7.40	5.45	2.44	1.73	0.39	699.17
150°C/80Hz	14.38	0.74	63.01	56.47	6.15	2.53	7.52	5.61	2.51	1.57	0.39	688.85
185°C/20Hz	10.78	0.66	63.25	55.94	6.09	2.70	7.49	5.25	2.33	1.42	0.33	630.38
185°C/55Hz(C)	12.43	0.72	62.88	56.67	6.21	2.50	7.62	5.51	2.47	1.57	0.40	689.71
185°C/55Hz(C)	11.41	0.69	63.40	55.88	6.13	2.73	7.46	5.45	2.42	1.55	0.35	655.32
185°C/90Hz	11.83	0.71	64.98	53.04	6.15	2.47	7.54	5.55	2.46	1.67	0.41	679.40
220°C/30Hz	10.28	0.63	63.02	56.29	6.17	2.80	7.66	5.62	2.50	1.55	0.37	657.90
220°C/80Hz	11.73	0.70	62.93	56.59	6.23	2.16	7.66	5.55	2.47	1.60	0.37	681.12
234°C/55Hz	10.93	0.63	64.38	53.99	6.22	2.45	7.46	5.50	2.45	1.69	0.36	651.02
S33												
136°C/55Hz	14.54	0.72	85.56	16.98	6.23	3.17	7.75	5.46	2.44	1.37	0.24	583.08
150°C/30Hz	10.50	0.71	86.27	16.04	6.21	2.61	7.69	5.67	2.53	1.26	0.24	568.46
150°C/80Hz	14.88	0.73	85.56	17.24	6.17	2.20	7.59	5.21	2.31	1.32	0.20	564.16
185°C/20Hz	10.57	0.64	83.95	19.89	6.08	2.48	7.71	4.11	1.83	1.46	0.29	627.80
185°C/55Hz(C)	12.05	0.72	85.11	17.88	6.19	2.80	7.91	5.54	2.45	1.22	0.20	508.26
185°C/55Hz(C)	10.90	0.70	85.57	17.07	6.22	2.61	7.42	5.85	2.60	1.08	0.15	593.40
185°C/90Hz	13.16	0.70	85.19	17.82	6.23	2.71	7.81	5.65	2.49	1.41	0.25	637.26
220°C/30Hz	10.20	0.58	80.75	24.38	6.05	2.37	7.93	6.14	2.74	1.38	0.23	708.63
220°C/80Hz	12.42	0.69	85.20	17.76	6.15	2.17	7.69	5.50	2.41	1.34	0.23	641.56
234°C/55Hz	11.21	0.61	84.29	19.01	6.11	2.51	7.67	5.80	2.56	1.33	0.24	616.62

C= center point, BD = bulk density, WI = whiteness index, YI = yellowness index, C/F = coarse/fine, TAA = total amino acids, TEAA = total essential amino acids, TP = total phenolics, TF = total flavonoids, DPPH = 2,2-diphenyl-1-picrylhydrazyl antioxidant activity

Table 3.2. Effect sizes and corresponding p and R^2 values of response variables of whole grain flour of the roasted S28 and S33 maize cultivars

Response variable	Effect	Effect size		p-value		R^2	
		S28	S33	S28	S33	S28	S33
Bulk density	TL	-6.13	-8.74	0.00	0.00	0.93	0.97
	SL	3.63	5.77	0.02	0.01		
	TQ	-1.17	-3.22	0.31	0.03		
	SQ	-0.82	-2.81	0.46	0.05		
	IL	1.60	3.42	0.19	0.03		
pH	TL	0.39	-2.14	0.72	0.10	0.68	0.69
	SL	1.29	1.52	0.27	0.20		
	TQ	1.47	-0.81	0.22	0.47		
	SQ	-1.28	-1.17	0.27	0.31		
	IL	0.20	0.68	0.85	0.54		
C/F ratio	TL	-1.03	-3.16	0.49	0.20	0.76	0.41
	SL	-1.91	-0.76	0.31	0.59		
	TQ	-0.40	-0.50	0.76	0.70		
	SQ	-0.60	-2.47	0.66	0.25		
	IL	-2.24	0.78	0.27	0.58		
Protein	TL	0.88	0.38	0.43	0.73	0.26	0.14
	SL	0.57	-0.36	0.60	0.74		
	TQ	-0.08	0.22	0.94	0.84		
	SQ	0.05	0.50	0.96	0.64		
	IL	-0.52	-0.32	0.63	0.07		
TAA	TL	14.17	2.00	0.05	0.30	0.52	0.37
	SL	4.27	1.71	0.15	0.34		
	TQ	-8.61	0.66	0.07	0.63		
	SQ	3.20	-3.02	0.19	0.20		
	IL	-2.71	-0.41	0.23	0.75		
TEAA	TL	0.91	1.60	0.53	0.36	0.43	0.35
	SL	2.23	1.25	0.27	0.43		
	TQ	0.51	0.65	0.70	0.63		
	SQ	-0.40	-2.80	0.76	0.22		
	IL	-1.41	-0.52	0.39	0.70		
Total phenolics	TL	-2.72	0.30	0.22	0.82	0.59	0.75
	SL	5.81	-1.13	0.12	0.92		
	TQ	8.82	1.78	0.07	0.33		
	SQ	-1.12	2.61	0.47	0.23		
	IL	6.90	-0.49	0.09	0.71		
Total flavonoids	TL	-0.15	0.07	0.91	0.95	0.40	0.72
	SL	1.41	-0.97	0.39	0.51		
	TQ	-0.31	1.42	0.81	0.39		
	SQ	0.18	2.22	0.86	0.27		
	IL	0.02	0.60	0.99	0.65		
DPPH	TL	0.20	1.56	0.88	0.36	0.26	0.70
	SL	1.19	-0.34	0.45	0.79		
	TQ	-1.01	0.91	0.50	0.53		
	SQ	0.15	1.49	0.90	0.38		
	IL	0.69	-0.52	0.62	0.69		

R^2 = coefficient of determination, TL = temperature linear effect, SL = speed linear effect, TQ = temperature quadratic effect, SQ = speed quadratic effect, IL = interaction linear effect

Optimisation of roasting conditions using desirability profiling

Desirability profile shows the levels of independent variables (roasting temperature and rotating speed) that produce the most desirable (maximum, minimum) predicted responses (moisture content, WI and YI). Response variables can be maximised, minimised or held constant during desirability profiling. The overall desirability function (*D*) was obtained by assigning predicted values a score which ranged from very undesirable (0) to very desirable (1) specified from individual desirability functions (*d$_i$*) of each of the response variables (Bezerra *et al.*, 2008). In plotting the desirability profiles, moisture content was maintained at ≤13.5% to obtain maximum WI and minimum YI at given roasting temperatures and rotating speeds. Guan and Yao (2008) reported that a prediction model that fits experimental data very well should have *R^2* value of ≥0.8 and a non-significant (*p* >0.05) lack-of-fit. Moisture content, WI and YI with *R^2* values of 0.82 and 0.90, 0.86 and 0.87, 0.86 and 0.88 for S28 and S33, respectively and non-significant lack-of-fits (Table 3.3) were considered for the optimisation of roasting conditions using desirability profiling. In addition to the above mentioned statistical parameters, these response variables were selected because moisture content of ≤13.5% was recommended to prevent fungal and microbial contamination of maize products (Humpf & Voss, 2004) and colour (WI, YI) of food influences consumers preference (Pathare *et al.*, 2013).

Temperature and speed combination that resulted in maximum WI and minimum YI values at moisture content between 12.2 and 13.4% was considered as the optimum roasting condition of each maize cultivar. For S28 (yellow maize) (Fig. 3.5), 189.9 °C and 90 Hz (Fig. 3.4) were considered as the optimum roasting condition to produce whole grain flour with high WI and low YI using FCCTR. Roasting temperature of 140.9 °C (Fig. 3.4) was found to produce whole grain flour of S33 (Fig. 3.5) with the highest WI and lowest YI and was considered as the optimum. Speeds of 48.0 Hz and 51.5 Hz (Fig. 3.4) were shown to produce the highest WI and lowest YI, respectively and their average (49.8 Hz) was considered as the optimum. Therefore, to produce the brightest whole grain flour of roasted S33 (white maize) using FCCTR, the optimum temperature and speed should be 140.9 °C and 49.8 Hz, respectively.

Table 3.3. Regression coefficients, R^2 and lack-of-fit's *p*-values for moisture content, WI and YI of roasted S28 and S33 maize cultivars

Response variable	Effect	Regression coefficient		R^2		*p*-value of lack-of-fit	
		S28	S33	S28	S33	S28	S33
Moisture	Mean	9.14503	24.86101	0.82	0.90	0.18	0.21
	$\beta_1 X_1$	-0.03410	-0.17748				
	$\beta_2 X_2$	0.25860	0.14892				
	$\beta_{11} X_1^2$	0.00015	0.00050				
	$\beta_{22} X_2^2$	-0.00061	0.00015				
	$\beta_{12} X_1 X_2$	-0.00084	-0.00062				
WI of flour	Mean	29.71478	93.59541	0.86	0.87	0.26	0.25
	$\beta_1 X_1$	0.28767	-0.02150				
	$\beta_2 X_2$	0.11757	-0.16239				
	$\beta_{11} X_1^2$	-0.00058	-0.00024				
	$\beta_{22} X_2^2$	0.00046	-0.00075				
	$\beta_{12} X_1 X_2$	-0.00077	0.00047				
YI of flour	Mean	114.31000	3.62247	0.86	0.88	0.23	0.30
	$\beta_1 X_1$	-0.49780	0.05208				
	$\beta_2 X_2$	-0.20510	0.22825				
	$\beta_{11} X_1^2$	0.00100	0.00031				
	$\beta_{22} X_2^2$	-0.00090	0.00130				
	$\beta_{12} X_1 X_2$	0.00140	-0.00223				

β = regression coefficient, X_1 = temperature linear effect, X_2 = speed linear effect, $X_1 X_2$ = interaction linear effect, X_1^2 = temperature quadratic effect, X_2^2 = speed quadratic effect, R^2 = coefficient of determination
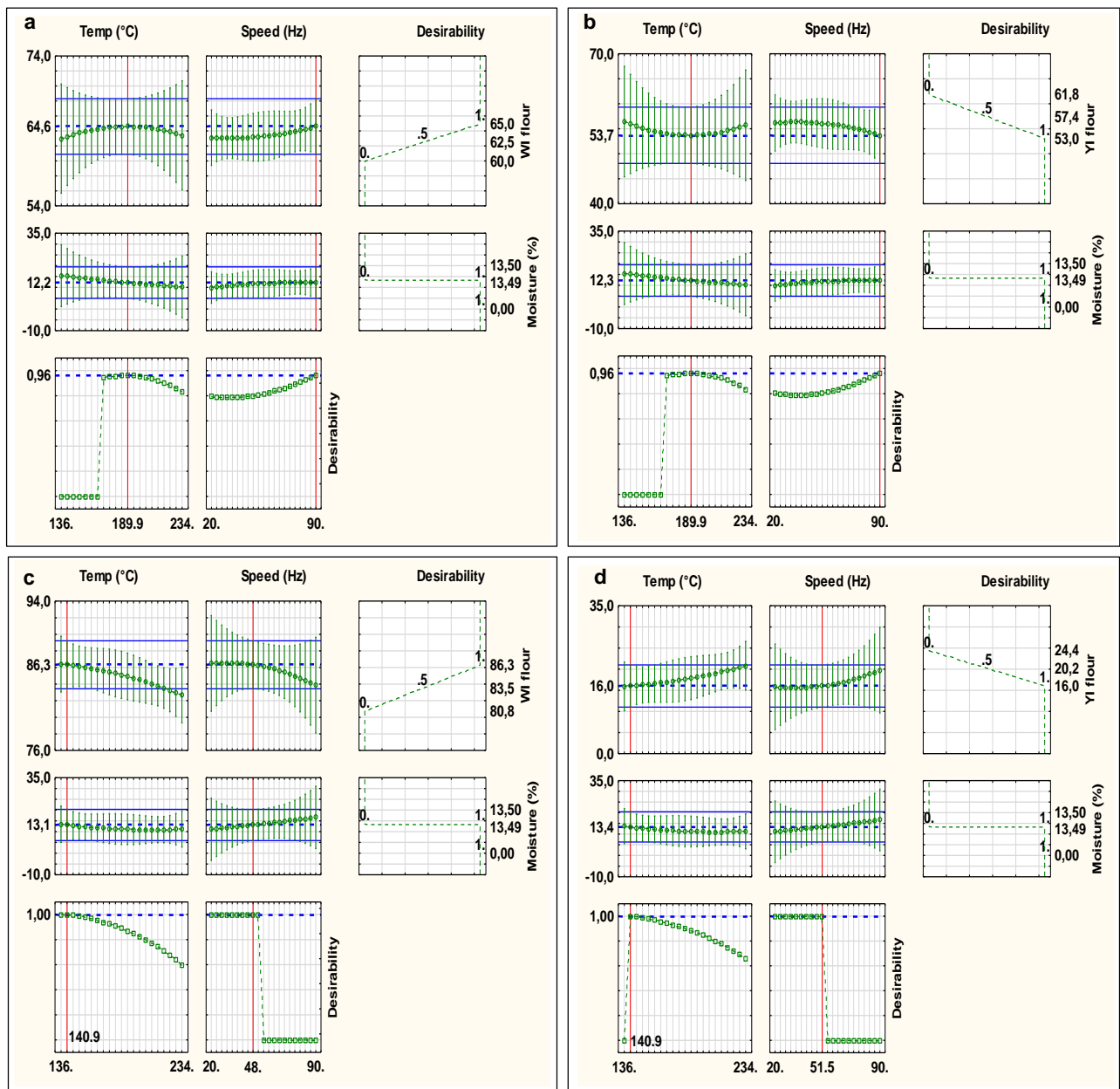
Figure 3.4. Profiles for predicted values and desirability of moisture content, (a) whiteness index [WI] and (b) yellowness index [YI] of S28, and (c) WI and (d) YI of S33 for the optimisation of roasting conditions (horizontal continuous blue lines in the graphs indicated confidence intervals used and the intersection of the horizontal dotted blue and vertical continuous red lines indicated the optimum roasting conditions).

59

Figure 3.5. Whole grain flour of the roasted (a) S28 and (b) S33 obtained using the mean optimum roasting conditions 189.9 °C/90 Hz and 140.9 °C/49.8 Hz, respectively.

Conclusions

FCR did not significantly affect the pH, kernel hardness, protein, amino acids profile, total phenolics and flavonoids and antioxidant activity of S28 and S33 within the experimental range used. Therefore, FCR did not have a negative effect on the nutritional properties and antioxidant content and activity of the maize cultivars. The R^2 value, which explains how prediction models fit experimental data, indicated that moisture content, WI and YI demonstrated good fit $(R^2 > 0.8)$. The desirability profiles of their prediction models showed that the optimum roasting conditions (roasting temperatures and rotating speeds) to produce whole grain flour with the best quality were 189.9 °C and 90 Hz for S28 (yellow maize) and 140.9 °C and 49.8 Hz for S33 (white maize), respectively. Further research should be conducted using two or more varieties of soft yellow and white maize grains for obtaining statistically better optimum roasting conditions.

References

AACC (1999). *Approved methods of the american association of cereal chemists international.* St. Paul, Minnesota, USA: AACC International.

Adom, K.K. & Liu, R.H. (2002). Antioxidant activity of grains. *Journal of Agricultural and Food Chemistry,* **50,** 6182-6187.

Alamprese, C., Ratti, S. & Rossi, M. (2009). Effects of roasting conditions on hazelnut characteristics in a two-step process. *Journal of Food Engineering,* **95,** 272-279.

Ayala-Rodríguez, A.E., Gutiérrez-Dorado, R., Milán-Carrillo, J., Mora-Rochín, S., López-Valenzuela, J.A., Valdez-Ortiz, A., Paredes-López, O. & Reyes-Moreno, C. (2009).

Nixtamalised flour and tortillas from transgenic maize (*Zea mays* L.) expressing amarantin: Technological and nutritional properties. *Food Chemistry,* **114,** 50-56.

Batterham, E., Lowe, R., Darnell, R. & Major, E. (1986). Availability of lysine in meat meal, meat and bone meal and blood meal as determined by the slope-ratio assay with growing pigs, rats and chicks and by chemical techniques. *British Journal of Nutrition,* **55,** 427-440.

Bezerra, M.A., Santelli, R.E., Oliveira, E.P., Villar, L.S. & Escaleira, L.A. (2008). Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta,* **76,** 965-977.

Blandino, M., Mancini, M.C., Peila, A., Rolle, L., Vanara, F. & Reyneri, A. (2010). Determination of maize kernel hardness: Comparison of different laboratory tests to predict dry-milling performance. *Journal of the Science of Food and Agriculture,* **90,** 1870-1878.

Bolade, M.K., Adeyemi, I.A. & Ogunsua, A.O. (2009). Influence of particle size fractions on the physicochemical properties of maize flour and textural characteristics of a maize-based nonfermented food gel. *International Journal of Food Science and Technology,* **44,** 646-655.

CAF (2014). Total amino acids content of hydrolysed samples. Stellenbosch University, South Africa. URL: http://academic.sun.ac.za/saf/services/services1.html Accessed 25/March/2014.

Cämmerer, B. & Kroh, L.W. (2009). Shelf life of linseeds and peanuts in relation to roasting. *LWT - Food Science and Technology,* **42,** 545-549.

Chung, H.-S., Chung, S.-K. & Youn, K.-S. (2011). Effects of roasting temperature and time on bulk density, soluble solids, browning index and phenolic compounds of corn kernels. *Journal of Food Processing and Preservation,* **35,** 832-839.

Costa, P., Jensen, A., Harmon, B. & Norton, H. (1976). The effects of roasting and roasting temperatures on the nutritive value of corn for swine. *Journal of Animal Science,* **42,** 365-374.

Craig, W.M. & Broderick, G.A. (1981). Effect of heat treatment on true digestibility in the rat, in vitro proteolysis and available lysine content of cottonseed meal protein. *Journal of Animal Science,* **52,** 292-301.

Das, I., Das, S. & Bal, S. (2004). Specific energy and quality aspects of infrared (IR) dried parboiled rice. *Journal of Food Engineering,* **62,** 9-14.

Durmaz, G. & Alpaslan, M. (2007). Antioxidant properties of roasted apricot (*Prunus armeniaca* L.) kernel. *Food Chemistry,* **100,** 1177-1181.

FDA (2015). pH values of various foods. U. S. Food and Drug Administration. New Hampshire, MD, USA. URL: http://www.fda.gov/Food/FoodborneIllnessContaminants/CausesOfIllnessBadBugBook/ucm 122561.htm Accessed 3/December/2014.

Fritz, T. (2013). Backgound and working principle (operation manual) of forced convection continuous tumble roaster (FCCTR). Bloemfontein, South Africa: Roastech.

Guan, X. & Yao, H. (2008). Optimization of viscozyme I-assisted extraction of oat bran protein using response surface methodology. *Food Chemistry,* **106,** 345-351.

Guillot, F.L., Malnoë, A. & Stadler, R.H. (1996). Antioxidant properties of novel tetraoxygenated phenylindan isomers formed during thermal decomposition of caffeic acid. *Journal of Agricultural and Food Chemistry,* **44,** 2503-2510.

Hefnawy, T.H. (2011). Effect of processing methods on nutritional composition and anti-nutritional factors in lentils (*Lens culinaris*). *Annals of Agricultural Sciences,* **56,** 57-61.

Hernandez, J., Heyd, B., Irles, C., Valdovinos, B. & Trystram, G. (2007). Analysis of the heat and mass transfer during coffee batch roasting. *Journal of Food Engineering,* **78,** 1141-1148.

Hoseney, R.C. (1994). *Principles of cereal science and technology.* St. Paul, Minnesota, USA: American Association of Cereal Chemists (AACC).

Hsu, C.-L., Chen, W., Weng, Y.-M. & Tseng, C.-Y. (2003). Chemical composition, physical properties, and antioxidant activities of yam flours as affected by different drying methods. *Food Chemistry,* **83,** 85-92.

Humpf, H.-U. & Voss, K.A. (2004). Effects of thermal food processing on the chemical structure and toxicity of fumonisin mycotoxins. *Molecular Nutrition and Food Research,* **48,** 255-269.

Jaramillo-Flores, M.E., González-Cruz, L., Cornejo-Mazón, M., Dorantes-Alvarez, L., Gutiérrez-López, G.F. & Hernández-Sánchez, H. (2003). Effect of thermal treatment on the antioxidant activity and content of carotenoids and phenolic compounds of cactus pear cladodes (*Opuntia ficus-indica*). *Food Science and Technology International,* **9,** 271-278.

Jenkins, P.J. & Donald, A.M. (1998). Gelatinisation of starch: A combined SAXS/WAXS/DSC and sans study. *Carbohydrate Research,* **308,** 133-147.

Jha, S.N. (2005). Mathematical simulation of roasting of grain. *Journal of Food Engineering,* **71,** 304-310.

Kahyaoglu, T. (2008). Optimization of the pistachio nut roasting process using response surface methodology and gene expression programming. *LWT - Food Science and Technology,* **41,** 26-33.

Karioti, A., Hadjipavlou-Litina, D., Mensah, M.L., Fleischer, T.C. & Skaltsa, H. (2004). Composition and antioxidant activity of the essential oils of *Xylopia aethiopica* (Dun) A. Rich. (Annonaceae) leaves, stem bark, root bark, and fresh and dried fruits, growing in Ghana. *Journal of Agricultural and Food Chemistry,* **52,** 8094-8098.

Kayacier, A. & Singh, R.K. (2003). Textural properties of baked tortilla chips. *LWT - Food Science and Technology,* **36,** 463-466.

Kayitesi, E., De Kock, H.L., Minnaar, A. & Duodu, K.G. (2012). Nutritional quality and antioxidant activity of marama–sorghum composite flours and porridges. *Food Chemistry,* **131,** 837-842.

Kayitesi, E., Duodu, K.G., Minnaar, A. & De Kock, H.L. (2010). Sensory quality of marama/sorghum composite porridges. *Journal of the Science of Food and Agriculture,* **90,** 2124-2132.

Lazou, A. & Krokida, M. (2010). Functional properties of corn and corn–lentil extrudates. *Food Research International,* **43,** 609-616.

Lee, S. & Lee, J. (2009). Effects of oven-drying, roasting, and explosive puffing process on isoflavone distributions in soybeans. *Food Chemistry,* **112,** 316-320.

Lemos, M.R.B., Siqueira, E.M.D.A., Arruda, S.F. & Zambiazi, R.C. (2012). The effect of roasting on the phenolic compounds and antioxidant potential of baru nuts [*Dipteryx alata* Vog.]. *Food Research International,* **48,** 592-597.

López-Martínez, L.X., Parkin, K.L. & Garcia, H.S. (2012). Effect of processing of corn for production of masa, tortillas and tortilla chips on the scavenging capacity of reactive nitrogen species. *International Journal of Food Science and Technology,* **47,** 1321-1327.

Maruatona, G.N., Duodu, K.G. & Minnaar, A. (2010). Physicochemical, nutritional and functional properties of marama bean flour. *Food Chemistry,* **121,** 400-405.

Mcglynn, W. (2015). *The importance of food ph in commercial canning operations.* Oklahoma, USA: Oklahoma Cooperative Extension Services.

Mcnaughton, J. & Reece, F. (1980). Effect of moisture content and cooking time on soybean meal urease index, trypsin inhibitor content, and broiler growth. *Poultry Science,* **59,** 2300-2306.

Mcniven, M.A., Hamilton, R.M.G., Robinson, P.H. & Deleeuw, J.W. (1994). Effect of flame roasting on the nutritional quality of common cereal grains for non-ruminants and ruminants. *Animal Feed Science and Technology,* **47,** 31-40.

Mendes, L.C., De Menezes, H.C., Aparecida, M. & Da Silva, A. (2001). Optimization of the roasting of robusta coffee (*C. canephora* Conillon) using acceptability tests and RSM. *Food Quality and Preference,* **12,** 153-162.

Milán-Carrillo, J., Gutiérrez-Dorado, R., Cuevas-Rodríguez, E., Garzón-Tiznado, J. & Reyes-Moreno, C. (2004). Nixtamalized flour from quality protein maize (*Zea mays* L.). Optimization of alkaline processing. *Plant Foods for Human Nutrition,* **59,** 35-44.

Murthy, K.V., Ravi, R., Bhat, K.K. & Raghavarao, K.S.M.S. (2008). Studies on roasting of wheat using fluidized bed roaster. *Journal of Food Engineering,* **89,** 336-342.

Nicoli, M., Anese, M. & Parpinel, M. (1999). Influence of processing on the antioxidant properties of fruit and vegetables. *Trends in Food Science and Technology,* **10,** 94-100.

Nyembwe, P., Minnaar, A., Duodu, K.G. & De Kock, H.L. (2015). Sensory and physicochemical analyses of roasted marama beans [*Tylosema esculentum* (Burchell) A. Schreiber] with specific focus on compounds that may contribute to bitterness. *Food Chemistry,* **178,** 45-51.

O'kennedy, K. (2011). *Characterisation of zein from south african maize of varying endosperm texture.* MSc Thesis, Stellenbosch University.

Oboh, G., Ademiluyi, A.O. & Akindahunsi, A.A. (2010). The effect of roasting on the nutritional and antioxidant properties of yellow and white maize varieties. *International Journal of Food Science and Technology,* **45,** 1236-1242.

Oliviero, T., Capuano, E., CäMmerer, B. & Fogliano, V. (2008). Influence of roasting on the antioxidant activity and hmf formation of a cocoa bean model systems. *Journal of Agricultural and Food Chemistry,* **57,** 147-152.

Özdemir, M., Açkurt, F., Yildiz, M., Biringen, G., Gürcan, T. & Löker, M. (2001). Effect of roasting on some nutrients of hazelnuts (*Corylus avellena* L.). *Food Chemistry,* **73,** 185-190.

Park, M., Kim, K. & Kim, J. (1993). Changes in the physicochemical properties of ginseng by roasting. *Journal of Ginseng Research,* **17,** 228-231.

Pathare, P.B., Opara, U.L. & Al-Said, F.a.-J. (2013). Colour measurement and analysis in fresh and processed foods: A review. *Food and Bioprocess Technology,* **6,** 36-60.

Pittia, P., Dalla Rosa, M. & Lerici, C.R. (2001). Textural changes of coffee beans as affected by roasting conditions. *LWT - Food Science and Technology,* **34,** 168-175.

Reyes-Moreno, C., Milán-Carrillo, J., Gutiérrez-Dorado, R., Paredes-López, O., Cuevas-Rodrıguez, E. & Garzón-Tiznado, J. (2003). Instant flour from quality protein maize (*Zea mays* L.). Optimization of extrusion process. *LWT-Food Science and Technology,* **36,** 685-695.

Rhim, J., Wu, Y., Weller, C. & Schnepf, M. (1999). Physical characteristics of a composite film of soy protein isolate and propyleneglycol alginate. *Journal of Food Science,* **64,** 149-152.

Saklar, S., Ungan, S. & Katnas, S. (2003). Microstructural changes in hazelnuts during roasting. *Food Research International,* **36,** 19-23.

Sharma, P. & Gujral, H.S. (2011). Effect of sand roasting and microwave cooking on antioxidant activity of barley. *Food Research International,* **44,** 235-240.

Sriperm, N., Pesti, G.M. & Tillman, P.B. (2011). Evaluation of the fixed nitrogen-to-protein (N: P) conversion factor (6.25) versus ingredient specific N: P conversion factors in feedstuffs. *Journal of the Science of Food and Agriculture,* **91,** 1182-1186.

USDA (2015). Corn production by country in 1000MT. United States Department of Agriculture. URL: http://www.indexmundi.com/agriculture/?commodity=corn Accessed 21/February/2015.

Uvere, P.O., Onyekwere, E.U. & Ngoddy, P.O. (2010). Production of maize-bambara groundnut complementary foods fortified pre-fermentation with processed foods rich in calcium, iron, zinc and provitamin a. *Journal of the Science of Food and Agriculture,* **90,** 566-73.

Uysal, N., Sumnu, G. & Sahin, S. (2009). Optimization of microwave–infrared roasting of hazelnut. *Journal of Food Engineering,* **90,** 255-261.

Wang, L., Chen, J., Xie, H., Ju, X. & Liu, R.H. (2013). Phytochemical profiles and antioxidant activity of adlay varieties. *Journal of Agricultural and Food Chemistry,* **61,** 5103-5113.

Wang, N., Hatcher, D.W., Tyler, R.T., Toews, R. & Gawalko, E.J. (2010). Effect of cooking on the composition of beans (*Phaseolus vulgaris* L.) and chickpeas (*Cicer arietinum* L.). *Food Research International,* **43,** 589-594.

Yang, J., Martinson, T.E. & Liu, R.H. (2009). Phytochemical profiles and antioxidant activities of wine grapes. *Food Chemistry,* **116,** 332-339.

Yazdanpanah, H., Mohammadi, T., Abouhossain, G. & Cheraghali, A.M. (2005). Effect of roasting on degradation of aflatoxins in contaminated pistachio nuts. *Food and Chemical Toxicology,* **43,** 1135-1139.

Youn, K.-S. & Chung, H.-S. (2012). Optimization of the roasting temperature and time for preparation of coffee-like maize beverage using the response surface methodology. *LWT - Food Science and Technology,* **46,** 305-310.

Žilić, S., Serpen, A., Akıllıoğlu, G., Gökmen, V. & Vančetović, J. (2012). Phenolic compounds, carotenoids, anthocyanins, and antioxidant capacity of colored maize (*Zea mays* L.) kernels. *Journal of Agricultural and Food Chemistry,* **60,** 1224-1231.

CHAPTER FOUR

Chapter 4

Effect of forced convection roasting on physicochemical and antioxidant properties of South African maize (*Zea mays* L.) hybrids and optimisation of roasting conditions for the production of whole grain meal

Abstract

The effect of roasting temperature and rotating speed (determining roasting time) during forced convection roasting on physicochemical and antioxidant properties of two South African white maize hybrids (H2G1; H7D1) was investigated and roasting conditions optimised. Minimum and maximum temperatures (136 and 234 °C) and rotating speeds (20 and 90 Hz) were selected to generate experimental runs using central composite design. The results showed that variation in temperature and speed did not significantly alter kernel hardness, protein content, total flavonoids and antioxidant activity of both hybrids. There was a significant decrease in whiteness index (WI) and increase in yellowness index (YI) of H7D1 meal with increase in temperature and decrease in speed. Total amino acids (TAA) content of H2G1 meal significantly decreased while that of H7D1 increased with increase in temperature and decrease in speed. Desirability profiles of prediction models of WI, YI and TAA suggested the following mean optimum roasting conditions: 185.0 °C, 65.5 Hz for H2G1 and 182.6 °C, 55.0 Hz for H7D1.

Introduction

The total global production of maize (*Zea mays* L.), the most cultivated cereal crop in the world, was about 990 million metric tons (MMT) in 2014 and South Africa was ranked the 8th largest producer with approximately 13.5 MMT (USDA, 2015). Most of the maize produced in developed countries such as USA is used for the production of animal feed and bio-ethanol with some used as raw materials for food products. Whereas in developing countries such as South Africa most of the maize cultivated is consumed as staple food by humans.

'Mielie pap' (maize porridge) is one of the major food products prepared using maize meal and consumed in Southern Africa. The maize meal used is not pregelatinised and does not contain bran and germ. Gelatinisation of native starch results in structural changes of the starch granules due to increase in temperature in the presence of water (Waigh *et al.*, 2000). The process is irreversible and needed in most industrial and culinary applications. Maize bran contains dietary fibre [hemicellulose (75%), cellulose (25%) and lignin (0.1%)] and phytochemicals (phenolics, phytic acid, tocotrienols, lignans and flavonoids), minerals and vitamins while the germ provides protein, oil (unsaturated fat), vitamins and minerals. Consumption of whole grain (including bran and germ) provides better diet quality and nutrients intake in adults (O'Neil *et al.*, 2010). Whole grain consumption was reported to significantly reduce obesity (Good *et al.*, 2008), stroke and hypertension (Steffen *et al.*, 2003), certain types of cancer (Schatzkin *et al.*, 2007), cardiovascular diseases (Jensen *et al.*, 2004) and type 2 diabetes mellitus (de Munter *et al.*, 2007). Phytochemicals in whole grains are believed to directly contribute to reducing and preventing diseases due to their antioxidant properties (Kennedy & Knill, 2003).

Heat-processing methods that can convert maize into preprocessed and finished food products include boiling, baking, nixtamalisation, extrusion and roasting. The selection of a heat-processing method depends on ingredients, environment, economy and traditions of people across the world. Roasting is a heat-processing technique that involves the use of dry hot-air (Oliviero *et al.*, 2008) resulting in various physicochemical, nutritional and phytochemical changes which can be desirable or undesirable. Enhancing the content and activity of antioxidants (Chung *et al.*, 2011), increasing flavour of end products (Lee & Lee, 2009), improving product shlef life and quality (Cämmerer & Kroh, 2009), removal of harmful substances (Yazdanpanah *et al.*, 2005) and efficiency of subsequent processing steps (Chung *et al.*, 2011) are some of the desirable changes. The undesirable changes are associated with decrease in nutritive values caused by the loss of essential amino acids through Maillard reaction, decrease in digestibility of proteins and carbohydrates and loss of vitamins (Özdemir *et al.*, 2001).

A novel grain processing technique [forced convection roasting (FCR)], involves forcing superheated steam (dry steam) through the grains while continuously being mixed and moved through a roasting chamber (Fritz, 2013). The FCR was developed with an option of using superheated steam to replace dry heat during the process of roasting. Continuous tumbling of the roasting chamber and the superheated steam generated by the forced convection continuous

tumble roaster (FCCTR) result in even roasting of the grains. FCR of cereal grains requires increase in moisture (tempering) before roasting. However, other crops such as some legumes with high oil and protein content do not require tempering. The physicochemical, nutritional, functional and antioxidant properties of marama bean (*Tylosema esculentum*) dry-heated (roasted) using FCCTR were extensively studied (Maruatona *et al.*, 2010; Kayitesi *et al.*, 2012; Nyembwe *et al.*, 2015). Significant increase in *in vitro* protein digestibility, water absorption capacity, and reduction in protein solubility and emulsifying capacity of the marama bean were reported. FCR with superheated steam did not show significant changes in physicochemical and antioxidant properties of Nigerian soft maize cultivars (S28, S33) (Chapter 3). However, for the South African hard maize hybrids (H2G1, H7d1), there was significant increase in total phenolics content of H2G1, but the physicochemical properties and antioxidant activities were not significantly affected.

Response surface methodology (RSM) is a statistical technique used for studying complex processes and it has been successfully used in different food processing optimisation procedures using central composite design (Mendes *et al.*, 2001; Reyes-Moreno *et al.*, 2003; Milán-Carrillo *et al.*, 2004; Kahyaoglu, 2008; Youn & Chung, 2012). RSM is used for studying the effect of and relationship between experimental factors (independent variables) and response (dependent) variables. It can also be used in empirical building of models for the optimisation of response variables using second-degree polynomial equation and desirability profiling. RSM saves experimental materials and time by providing useful and reliable information with the lowest possible number of experiments. The aim of this study was to investigate the effect of FCR on physicochemical and antioxidant properties of South African maize hybrids and to optimise the roasting conditions using RSM, for the production of whole grain meal.

Materials and methods

Materials

Two white maize hybrids, H2G1 and H7D1 (5 kg each) were kindly provided by PANNAR Seeds (Greytown, KwaZulu-Natal, South Africa). The two maize hybrids were cultivated in different provinces of South Africa, H2G1 (10.77% moisture) in Greytown, KwaZulu-Natal and H7D1 (11.05% moisture) in Delmas, Npumalanga. Uninfected sample of uniform kernel size were cleaned by removing foreign materials and broken kernels and kept in airtight plastic containers at ambient temperature prior to roasting.

Chemicals

Acetone, methanol, ethyl acetate, sodium carbonate (Na_2CO_3), sodium nitrite ($NaNO_2$), aluminium chloride ($AlCl_3$), sodium hydroxide (NaOH), sodium acetate trihydrate ($C_2H_3NaO_2 \cdot 3H_2O$), glacial acetate ($C_2H_4O_2$) and hydrochloric acid (HCl); Folin-Ciocalteau and DPPH (2,2-diphenyl-1-picrylhydrazyl) reagents and gallic acid, ascorbic acid and catechin standards were purchased from Sigma-Aldrich (St. Louis, USA). Alfalfa standard was purchased from Leco Corporation (Leco

Africa, Kempton Park, South Africa). Ultra-derivatisation Kit AccQ-Tag was purchased from Waters (Waters Corporation, Massachusetts, USA).

Tempering of maize kernels

As required for the operation of the FCCTR, the moisture content of the maize kernels was increased to 8 – 20% by tempering using the American Association of Cereal Chemists International (AACCI) Approved Method 26-95.01 as described by (Chapter 3). The quantity of water required (Eq. 1) was added to each maize sample (200 g/run) in a screw capped plastic container and stored at room temperature for 72 h. To ensure even absorption of moisture throughout the kernels, the container was shaken at 6 h interval.

$$\text{Water to add (mL)} = \left[\frac{100 - \text{initial moisture (\%)}}{100 - \text{required moisture (\%)}} - 1\right] \times \text{sample weight (g)} \tag{1}$$

Experimental design

Ten experimental runs (Table 4.1) of roasting temperature (X_1) and rotating speed (X_2) were generated using a central composite design with two factorial levels (minimum and maximum), two center points (C) and two axial points (minimum and maximum) based on roasting temperature (150 and 220 °C) and rotating speed (determining roasting time) (30 and 90 Hz) limits obtained from preliminary roasting experiments. The response variables (Y) considered were moisture content, bulk density, colour [whiteness index (WI) and yellowness index (YI)], pH, kernel hardness [coarse/fine (C/F) ratio], protein content, amino acids profile [total amino acids (TAA) and total essential amino acids (TEAA)], total phenolics, total flavonoids and DPPH antioxidant activity. Prediction models of the response variables were obtained using the second-degree polynomial equation (Eq. 2):

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{12} X_1 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 \tag{2}$$

where β_o is constant (intercept), β_1 and β_2 are linear coefficients, β_{11} and β_{22} are quadratic coefficients and β_{12} is the coefficient of interaction.

Forced convection roasting

The cleaned, tempered maize kernels (200 g/run) were roasted in a FCCTR, model R100E (Roastech, Bloemfontein, South Africa) according to the generated experimental runs. The roaster was operated at 150 °C and 20 Hz and tempered maize grains (2 kg of a different hybrid) was roasted to generate superheated steam in the roasting chamber. Then the 200 g/run experimental samples were roasted. The roasted 200 g/run maize samples were cooled to room temperature and milled using a Cyclone Laboratory Mill, model 3100 (Perten Instruments, Hagersten, Sweden)

fitted with 0.8 mm sieve. The meal obtained were stored in screw capped plastic containers and refrigerated prior to analyses.

Determination of moisture content

Moisture content of the roasted maize flour was determined in triplicate as described in the AACCI Approved Method 44–19.01 (AACC, 1999). About 2 ± 0.001 g of the flour was heated in an aluminium dish for 2 h at 135 °C in an oven, model EM10 (CHOPIN Technologies, Cedex, France) and the moisture content was calculated using equation 3:

$$\text{Moisture (\%)} = \frac{\text{loss in moisture} \times 100}{\text{weight of sample}} \qquad (3)$$

Determination of bulk density

The bulk density of the roasted maize was determined in triplicate (Chung *et al.*, 2011). Maize kernels were weighed in a container of known volume using a laboratory balance, model ATA620 (Axis Sp, Gdansk, Poland) and the bulk density calculated (Eq. 4).

$$\text{Bulk density (g/cm}^3) = \frac{\text{weight}}{\text{volume}} \qquad (4)$$

Determination of colour

The colour of the roasted maize flour was measured in triplicate as CIELAB coordinates (*L**, *a**, *b**) using a colour-guide Gloss 45/0 spectrophotometer (BYK-Gardner, Geretsried, Germany). Whiteness index (WI) and yellowness index (YI) where calculated using equations 5 and 6 (Pathare *et al.*, 2013).

$$\text{WI} = 100 - [(100 - L*)^2 + a*^2 + b*^2]^{0.5} \qquad (5)$$

$$\text{YI} = \frac{142.86\, b*}{L*} \qquad (6)$$

Determination of pH

Triplicate measurement of pH of the roasted maize flour was done using the AACCI Approved Method 02–52.01 (AACC, 1999) with minor modifications. The meal (10 g) was weighed into a glass vial, 100 mL distilled water added and sonicated in a 40 KHz Ultrasonic Water Bath, model DC400H (MRC Ltd, Tel-Aviv, Israel) for 20 min. The mixture was allowed to stand for 10 min and the supernatant carefully decanted. Three different buffer solutions (pH 4, 7 and 9.2) were used for calibration and the pH was immediately measured while stirring using a pH meter, model BASIC 20+ (Crison, Barcelona, Spain).

Determination of kernel hardness

Kernel hardness of the roasted maize was determined in duplicate as coarse/fine (C/F) ratio by means of the particle size index (PSI) method (O'Kennedy, 2011). The roasted maize kernel (50 g) was milled using the Cyclone Laboratory Mill, model 3100 (Perten Instruments, Hagersten, Sweden) fitted with a 1 mm sieve to obtain maize flour. Ten grams of the flour were weighed onto the 150 μm sieve and 10 g of whole wheat was put onto each of the 150 and 75 μm sieves. Two sets of sieves and pans were stacked together on a Retsch Tap Sieve Shaker, model AS200 (Retsch, Haan, Germany) for 10 min. The whole wheat kernels were added to obtain effective sieving of the flour. After sieving, fine maize flour adhering to the bottom of the 150 μm sieve were brushed gently into the 75 μm sieve and fine flour adhering to the bottom of the 75 μm were brushed gently into the receiving pan. Three fractions PSI_1, PSI_2 and PSI_3 (Eqs. 7, 8 and 9) were determined and the C/F ratio calculated (Eq. 10). The higher the C/F ratio value the harder the maize kernel.

$$PSI_1 = \frac{W_1 - (W_{150\mu m \ sieve} + W_{wheat \ in \ 150\mu m \ sieve})}{W_{maize \ flour}} \tag{7}$$

$$PSI_2 = \frac{W_2 - (W_{75\mu m \ sieve} + W_{wheat \ in \ 75\mu m \ sieve})}{W_{maize \ flour}} \tag{8}$$

$$PSI_3 = \frac{(W_3 - W_{pan})}{W_{maize \ flour}} \tag{9}$$

$$C/F = \frac{PSI_1}{(PSI_2 + PSI_3)} \tag{10}$$

where W_1 = weight of 150 μm sieve and its content after sieving; W_2 = weight of 75 μm sieve and its content after sieving; W_3 = receiving pan and its content after sieving; $W_{150\mu m \ sieve}$ = weight of empty 150 μm sieve; $W_{75\mu m \ sieve}$ = weight of empty 75 μm sieve; $W_{wheat \ in \ 150\mu m \ sieve}$ = weight of wheat kernels in 150 μm sieve; $W_{wheat \ in \ 75\mu m \ sieve}$ = weight of wheat kernels in 75 μm sieve; W_{pan} = weight of empty pan; and $W_{maize \ meal}$ = weight of maize flour.

Determination of crude protein

The crude protein content of the roasted maize was determined in duplicate by Dumas combustion method as described in AACCI Approved Method 46–30.01 (AACC, 1999) using a Leco, model FP-528 (Leco Africa, Kempton Park, South Africa). Calibration of the instrument was done using an alfalfa standard with a known nitrogen content of 3.38 ± 0.04%. A series of blank determinations were performed in order to get rid of any element in the instrument. Calibration of the instrument was done using an alfalfa standard with a known nitrogen content of 3.38 ± 0.04%. Alfalfa standard and the roasted maize flour (0.5 g each) were weighed onto a tin foil cup, twisted, rolled into an egg shape and loaded into the instrument. For the pyrolysis of samples in pure

oxygen (99.9%), 850 °C was used as combustion temperature. Crude protein was obtained by multiplying the nitrogen content with the conversion factor 5.68 (Sriperm *et al.*, 2011). Calculated crude protein content was expressed on a 12% moisture basis (Eq. 11), where APC = adjusted protein content; MPC = measured protein content; FMC = final moisture content (12%); and OMC = original moisture content of sample.

$$\text{APC (\%)} = \text{MPC} * \frac{100 - \text{FMC}}{100 - \text{OMC}} \tag{11}$$

Determination of amino acids profile

The roasted maize flour (100 mg) was hydrolysed overnight with 6 mL of 6 N 15% phenolic HCl at 110 °C. Amino acids in the hydrolysates were determined in duplicate using liquid chromatography mass spectrometry (LC/MS) (CAF, 2014). The LC was performed in a Waters API Quattro Micro UPLC (Waters Corporation, Massachusetts, USA) using Waters AccQ-Tag Ultra Derivatisation Kit (Waters Corporation, Massachusetts, USA). The column temperature was maintained at 36 °C and the detection source was ESI$^+$ (electrospray ionisation). The solvents Eluent A2 (100 mL eluent A concentrate [6-aminoquinolyl-N-hydroxysuccinimidyl carbamate + acetonitrile] and 900 mL distilled water) and Eluent B (acetonitrile) were used. The MS analysis was done using a Waters ACQUITY Tandem Triple Quadrupole Spectrometer (Waters Corporation, Massachusetts, USA) with capillary voltage set at 3.5 kV and 15 V for cone voltage. The source and desolvation temperatures were set at 120 and 350 °C, and desolvation and cone gases at 350 and 50 L/h, respectively. Tryptophan, glutamine and asparagine were not determined out of the twenty naturally occurring amino acids.

Extraction of phenolic compounds

A slightly modified method of Wang *et al.* (2013) was used for extraction of free and bound phenolics. For free phenolic compounds, 1 ± 0.001 g of the roasted maize flour was weighed into a glass vial, 15 mL of 60% chilled aqueous acetone added and sonicated for 10 min at 20 °C in the 40 KHz ultrasonic water bath. The mixture was centrifuged in an Eppendorf centrifuge, model 5810R (Eppendorf AG, Hamgurg, Germany) for 10 min at 2500 g and 4 °C, supernatant collected and the residue re-centrifuged twice with 15 mL chilled aqueous acetone. The supernatants were pooled together and evaporated at ambient temperature to dryness. The extract was reconstituted in 5 mL 70% aqueous methanol. For bound phenolic compounds, the residue above was digested with 10 mL of 2 M NaOH for 1 h at ambient temperature. The digest was neutralised with 6 M HCl to a pH between 1.45 and 1.55 and extracted with 15 mL absolute ethyl acetate 4 times by centrifuging for 10 min at 2500 g and 4 °C. The ethyl acetate extracts were pooled together, evaporated to dryness and reconstituted in 5 mL of 70% methanol. Each of the free and bound reconstituted extracts were pooled together, filtered and stored (-80 °C) prior to analysis.

Determination of total phenolics content

Triplicate determination of total phenolics content was done using the Folin-Ciocalteau method (Žilić *et al.*, 2012). Standard and extract (100 µL each) were put into labelled Eppendorf tubes and 400 µL of distilled water added. The mixture was neutralised with 1.25 mL of 20% aqueous Na_2CO_3, allowed to stand in the dark for 40 min at room temperature and the absorbance measured using a Helios Omega UV-vis spectrophotometer (Thermo scientific technologies, Madison, USA) at 725 nm against an absolute methanol blank. Total phenolics content was expressed as gram of gallic acid equivalent per 100 g of dry matter (g GAE/100 g DM) using a gallic acid standard curve.

Determination of total flavonoids content

The total flavonoids content was determined (Yang *et al.*, 2009) in triplicate. The standard and extract (250 µL each) were put into a centrifuge tube and 1.25 mL of distilled water added. About 75 µL of 5% $NaNO_2$ was added, the mixture shaken and allowed to stand for 5 min in the dark at room temperature. About 150 µL of 10% $AlCl_3$ was added, the mixture shaken and kept in the dark for 6 min. 1 M NaOH (500 µL) and 775 µL of distilled water were added and absorbance measured at 510 nm. The total flavonoids content was expressed as milligram of catechin equivalent per gram of dry matter (mg CE/g DM).

Determination of antioxidant activity

The DPPH radical scavenging activity was determined in triplicate as described by Karioti *et al.* (2004). The standard and extract (20 µL each) were put into Eppendorf tube, 800 µL of absolute methanol added and the mixture shaken. Solution of 0.1 mM DPPH (1 mL) was added, the mixture shaken and kept in the dark for 60 min at room temperature. The absorbance was measured at 517 nm. DPPH antioxidant activity was expressed as millimolar ascorbic acid equivalent per gram of dry matter (mM AAE/g DM).

Statistical analysis

The average values of the response variables were subjected to analysis of variance (ANOVA), partial F-test and regression analysis using Statistica version 12 (StatSoft Inc, Oklahoma, USA). Regression coefficients, standardised effect estimates (effect sizes) and *p*-values of linear, quadratic and interaction terms for X_1 and X_2 were determined. Significance of effects (linear, quadratic and interaction) of X_1 and X_2 on each of the response variables was expressed as effect size at 95% confidence interval. Prediction models (fitted response surface plots) were determined using the second-degree polynomial equation. Coefficient of determination (R^2) was used to compare variations as a result of differences in experimental treatments with variations due to errors in measurement of the response variables (Bezerra *et al.*, 2008). Desirability profiling was used for the determination of optimum roasting conditions.

Results and discussion

ANOVA and RSM data analyses

The linear, quadratic and interaction effects of X_1 and X_2 on the response variables were explained using the effect size and corresponding *p*-values. Standardised Pareto charts were used to show the significance of the effects of roasting temperature and rotating speed on some response variables where crossing the vertical red line by a bar (*p* =0.05) indicated significant effect otherwise not significant (*p* >0.05). The higher the effect size the stronger the level of significance. Positive and negative effect sizes showed positive and negative relationships with the dependent variable. Graphical representation of the prediction model was presented as three-dimensional (3-D) fitted response surface plot. Regression coefficient, R^2 and *p*-value of lack of fit were used to indicate how well the prediction model generated fits the experimental data. Prediction model of each response variable was calculated using their regression coefficients (*β₀, β₁, β₂, β₁₂, β₁₁,* and *β₂₂*) in the second-degree polynomial equation. For example, the prediction model of TEAA content of H2G1 was deduced using equation 12 where Y = TEAA (g/100 g), X_1 = temperature (ºC) and X_2 = speed (Hz).

$$Y = 5.60753 - 0.02338X_1 - 0.02168X_2 + 0.00013X_1X_2 + 0.00004X_1^2 - 0.00002X_2^2 \tag{12}$$

Good fit of a prediction model with experimental data is indicated by R^2 value of ≥0.8 (Guan & Yao, 2008) and a non-significant (*p* >0.05) lack-of-fit. The prediction models for YI and TEAA of H2G1, and WI and TAA of H7D1 (Fig. 4.1) at the recommended moisture content (≤13.5%) were used for the optimisation of roasting conditions using desirability profiling.

75
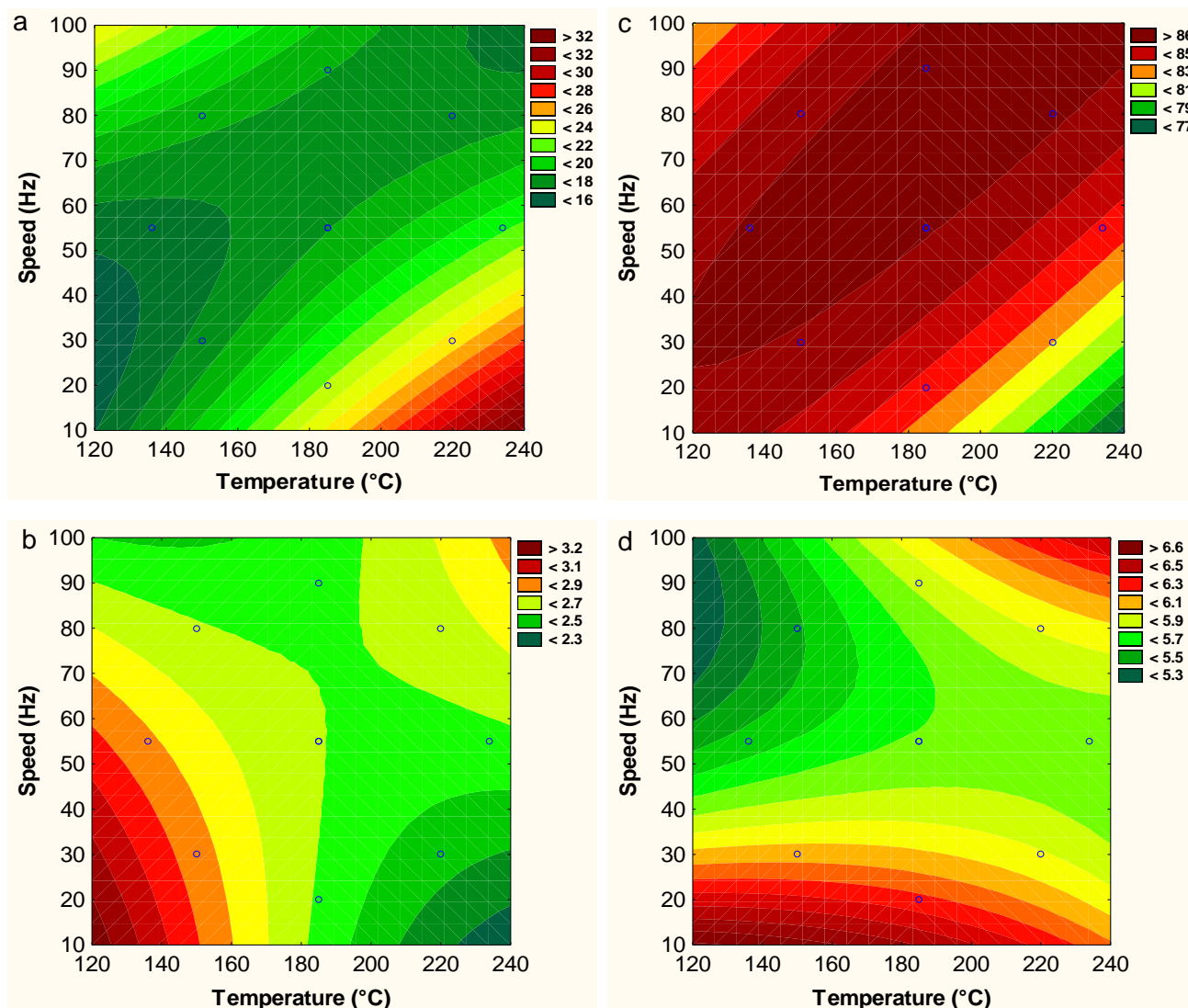
Figure 4.1. Fitted response surface plots of (a) yellowness index [YI] and (b) total essential amino acids [TEAA] for H2G1 and (c) whiteness index [WI] and (d) total amino acids [TAA] for H7D1 at varying roasting temperatures and rotating speeds.

Effect of temperature and speed on the response variables

Moisture content

Table 4.1 shows the moisture content of the roasted H2G1 and H7D1 samples which ranged from 10.62 to 14.64 and 10.72 to 14.64%, respectively. The prediction models of moisture content fitted the experimental data very well with an R^2 of 0.86 for each hybrid and non-significant ($p > 0.05$) lack-of-fit (Table 4.3). Roasting temperature showed a significant ($p \leq 0.05$) linear effect on the moisture content of H2G1 and H7D1 with negative effect sizes of -2.86 and -3.01 (Fig. 4.2), respectively which indicated significant decrease in moisture content with increase in temperature. Preliminary roasting experiments showed that the lower the rotating speed the greater the extent of roasting and the higher the moisture loss of the maize (result not shown). Decrease in moisture content with decrease in rotating speed was not significant in both hybrids which indicated that

temperature has greater impact on moisture loss compared to speed. The quadratic effects of temperature and speed as well as linear interaction effect on moisture content of the two maize hybrids were not significant (Fig. 4.2). The importance of moisture content in predicting the shelf life of food products, respiration and activity of spoilage microorganisms has been corroborated. Hoseney (1994) reported that fungal growth was terminated at moisture content of <14% for cereal grains. The moisture content of whole grain maize and products should be ≤13.5% for effective storage (Humpf & Voss, 2004). The recommended moisture content thus always needs to be taken into consideration during the optimisation of roasting conditions of maize grains.

Bulk density

The bulk density of the roasted H2G1 and H7D1 ranged from 0.57 to 0.72 and 0.58 to 0.72 g/cm^3 (Table 4.1), respectively with R^2-values of 0.89 and 0.99 (Table 4.2). The bulk density of roasted Korean maize kernels ranged between 0.52 to 0.79 g/cm^3 using an electric rotary roaster (Chung *et al.*, 2011) which agrees with the result of the present study. Linear effects of both roasting temperature and rotating speed on the bulk density of H2G1 and H7D1 were significant (Table 4.2). The linear temperature effects had negative effect sizes (-3.87 and -17.33) for H2G1 and H7D1, respectively, while those of linear speed effects were positive (2.73 and 15.02) (Table 4.2). This showed that bulk density significantly decreased in both hybrids with increase in roasting temperature and decrease in rotating speed. The higher effect size for H7D1 indicated greater impact of increase in temperature and decrease in speed on reducing bulk density compared to those for H2G1. The quadratic effect of temperature and speed as well as linear interaction effect were not significant on the bulk density of H2G1 but significant on that of H7D1. Bulk density is an important physical property of preprocessed cereals for storage, transportation and marketing. Decrease in bulk density was shown to be due to combined effects of kernel expansion, moisture loss, increase in volume, development of internal pores and decrease in weight of the maize kernels due to heating (Jha, 2005). The decrease in density observed in roasted hazelnut grains was caused by increase in intercellular spaces, cell wall separation, disruption of cellular cytoplasmic network and aggregation and swelling of protein bodies (Saklar *et al.*, 2003). A study by Murthy *et al.* (2008) on the effects of fluidized bed roasting indicated significant reduction in bulk density of wheat with increase in temperature which corresponded with the present finding.

Colour

WI is indicated on a scale from 0 to 100, which combines lightness (*L**) and yellow-green (*a** and *b**) colour into a single value (Pathare *et al.*, 2013). Consumers usually prefer whiter meal and the nearer the WI value to 100 the whiter the meal. The WI of the meal of roasted H2G1 and H7D1 ranged from 79.34 to 85.73 and 82.60 to 86.88 (Table 4.1), respectively, with R^2-values of 0.75 (Table 4.2) and 0.87 (Table 4.3) and non-significant (*p* >0.05) lack-of-fit. Linear effects of temperature and speed, quadratic effects of temperature and speed as well as interaction effect on

the WI of H2G1 were not significant (Table 4.2) which showed that changes in roasting temperature and rotating speed did not significantly alter the WI. For H7D1, all the effects (linear, quadratic and interaction) of temperature and speed on WI were significant (Fig. 4.2) where the effect sizes of linear effects of temperature and speed were -36.63 and 43.51, respectively. This indicated significant (p ≤0.05) increase in WI of H7D1 with decrease in temperature and speed. Maintenance of WI of H2G1 and increase in that of H7D1 could be associated to reduction in production of Maillard reaction products due to the replacement of dry hot air with superheated steam in the roasting chamber of the FCCTR.

Product degradation and scorching due to heat processing are associated with increase in yellowness and can be measured by YI (Pathare *et al.*, 2013). Table 4.1 shows the result of YI of H2G1 and H7D1, which ranged from 17.26 to 26.35 and 15.99 to 22.16, respectively. The R^2 values of H7D1 and H2G1 were 0.88 (Table 4.2) and 0.83 (Table 4.3), respectively with non-significant lack-of-fit. Linear effects of temperature and speed, quadratic effects of temperature and speed as well as interaction effect on the YI of H7D1 were significant (p ≤0.05) (Table 4.2). Effect sizes of 3.06 and -3.48 for linear temperature and speed effects, respectively on the YI of H7D1 were observed which showed significant increase in YI with increase in temperature and decrease in speed. For H2G1, all the effects of temperature and speed were not significant (p >0.05) on the YI (Fig. 4.2) which could also be attributed to minimising Maillard reaction by the superheated steam.

pH

The result of pH for H2G1 and H7D1 was presented in Table 4.1 which ranged from 6.07 to 6.27 and 6.09 to 6.32, with R^2 values for the prediction models of 0.69 and 0.87 (Table 4.2), respectively. Linear effects of temperature and speed, quadratic effects of temperature and speed as well as interaction effect on the pH of both hybrids were not significant (Table 2). This finding was similar to that reported in Chapter 3 on the pH of Nigerian maize cultivars (S28; S33). Therefore, FCR did not result in a decrease in pH in contrast to the finding of Chung *et al.* (2011) who reported significant decrease in pH of electric rotary roasted maize with increase in temperature (160 to 240 °C) and time (0 to 50 min). The value of pH of maize, a measure of acidity (free hydrogen ions), ranged between 6.0 and 7.2 (FDA, 2015). Heat-processing conditions that lower the pH value of maize grains to below 6.0 (increase in acidity) would have a negative effect. Hot air roasting of coffee beans at high temperatures >190 °C was associated with chemical changes such as hydrolysis, polymerisation and oxidation reactions (Hernandez *et al.*, 2007). These chemical reactions were responsible for decreasing the pH of roasted grains resulting in increased acidity of the roasted products. Similarly, roasting ginseng seeds at high temperature greater than 190 °C caused the conversion of sugars to acidic compounds (Park *et al.*, 1993) which also led to decrease in pH. Maintaining the pH of roasted maize meal by FCR could be attributed to the replacement of dry hot air with superheated steam during the roasting process.

This might be responsible for preventing pyrolytic reactions and conversion of sugars to acidic compounds and production of Maillard reaction products responsible for decrease in pH (Park *et al.*, 1993).

Kernel hardness

Maize kernel hardness is a very important quality parameter for maize classification, marketing and processing. Dry milling of maize grains produces different forms of flour, grits and meals which can be processed further into snacks, breakfast cereals and extruded products (Lee *et al.*, 2005). The kernel hardness of roasted H2G1 and H7D1 samples was expressed as C/F ratio and ranged from 2.14 to 3.17 and 2.21 to 3.32 (Table 4.1), with R^2-values of 0.87 and 0.57, respectively (Table 4.2). C/F ratio accurately and objectively provides an indirect but precise estimation of the hard and soft fractions of endosperm (Blandino *et al.*, 2010) which defines kernel hardness. Linear effects temperature and speed as well as quadratic effects of temperature and speed on C/F ratio of H2G1 were not significant ($p > 0.05$) but the linear interaction effect was, indicating that there was no significant change in kernel hardness of H2G1 hybrid with variation in roasting temperature and rotating speed. Increase in roasting temperature significantly ($p \leq 0.05$) increased kernel hardness of H7D1 hybrid with positive effect size (1.14). Linear and quadratic effects of speed as well as the linear interaction effect of temperature and speed on the kernel hardness of H7D1 were not significant (Table 4.2). The reason for increase in kernel hardness of H7D1 with increase in roasting temperature is not clear.

Crude protein

The crude protein content of roasted H2G1 and H7D1 samples at 12% moisture basis ranged from 8.76 to 9.07 and 8.62 to 9.09 % (Table 4.1), with R^2-values of 0.52 and 0.47 for the prediction models (Table 4.2), respectively. Linear effects of temperature and speed, quadratic effects of temperature and speed as well as interaction effect on protein content of both hybrids were not significant ($p > 0.05$) except the linear temperature effect of H7D1, which was significant with a negative effect size of -0.74 (Table 4.2). This showed that there was no significant variation in protein content of H2G1 with changes in roasting temperature and rotating speed but increase in temperature significantly decreased that of H7D1. Total protein content of lentils did not significantly change due to autoclaving, boiling and microwave cooking (Hefnawy, 2011). McNiven *et al.* (1994) reported that flame roasting of corn at roasting temperatures between 80 and 160 °C did not significantly affect the protein content. The decrease in protein content of H7D1 could be due to Maillard reaction between amino acids of the protein and reducing sugars of carbohydrate at higher temperatures (Nursten, 2005).

Amino acids profile

Total amino acids (TAA) of the roasted H2G1 and H7D1 samples ranged from 4.95 to 6.44 and 5.35 to 6.30 g/100g, whereas total essential amino acids (TEAA) were from 2.47 to 2.89 and 2.38 to 3.83 g/100g, respectively (Table 4.1). The R^2-values of prediction models of TAA of H2G1 and TEAA of H7D1 were 0.68 and 0.65 (Table 4.2) while those of TEAA of H2G1 and TAA of H7D1 were 0.87 and 0.86, respectively (Table 4.3). The TEAA consisted of arginine, histidine, valine, threonine, isoleucine, leucine, lysine, phenylalanine and methionine while the TAA comprised of TEAA, serine, glycine, aspartate, glutamate, alanine, proline, cysteine and tyrosine. Linear, quadratic and interaction effects of temperature and speed on TAA of H2G1 (Table 2) and H7D1 (Fig. 4.2) were significant ($p \leq 0.05$), but the linear temperature effect of H7D1 which was not ($p > 0.05$). The effect sizes of linear temperature and speed effects on TAA of H2G1 were -32.56 and 26.23, respectively which indicated significant decrease with increase in roasting temperature and decrease in rotating speed. For H7D1, the effect size of temperature and speed linear effects were 14.17 and -28.49, respectively, which indicated significant increase in TAA with increase roasting temperature and decrease in speed. The TEAA content of H2G1 significantly decreased with increase in temperature while variation in speed did not cause significant change (Fig. 4.2). There was significant increase in TEAA of H7D1 with decrease in speed whereas variation in temperature did not significantly affect the TEAA content (Table 4.2). Decrease in TAA and TEAA observed in H2G1 might be due to loss of arginine, lysine, serine and threonine because of heating as reported for cotton-seed, meat and soybean meals (McNaughton & Reece, 1980; Craig & Broderick, 1981; Batterham *et al.*, 1986). Most of the people in developing countries depend on plants products for consumption and economic purposes, therefore enhancing plants such as maize with essential amino acids (Ufaz & Galili, 2008) or preventing significant lose would be of great benefit.
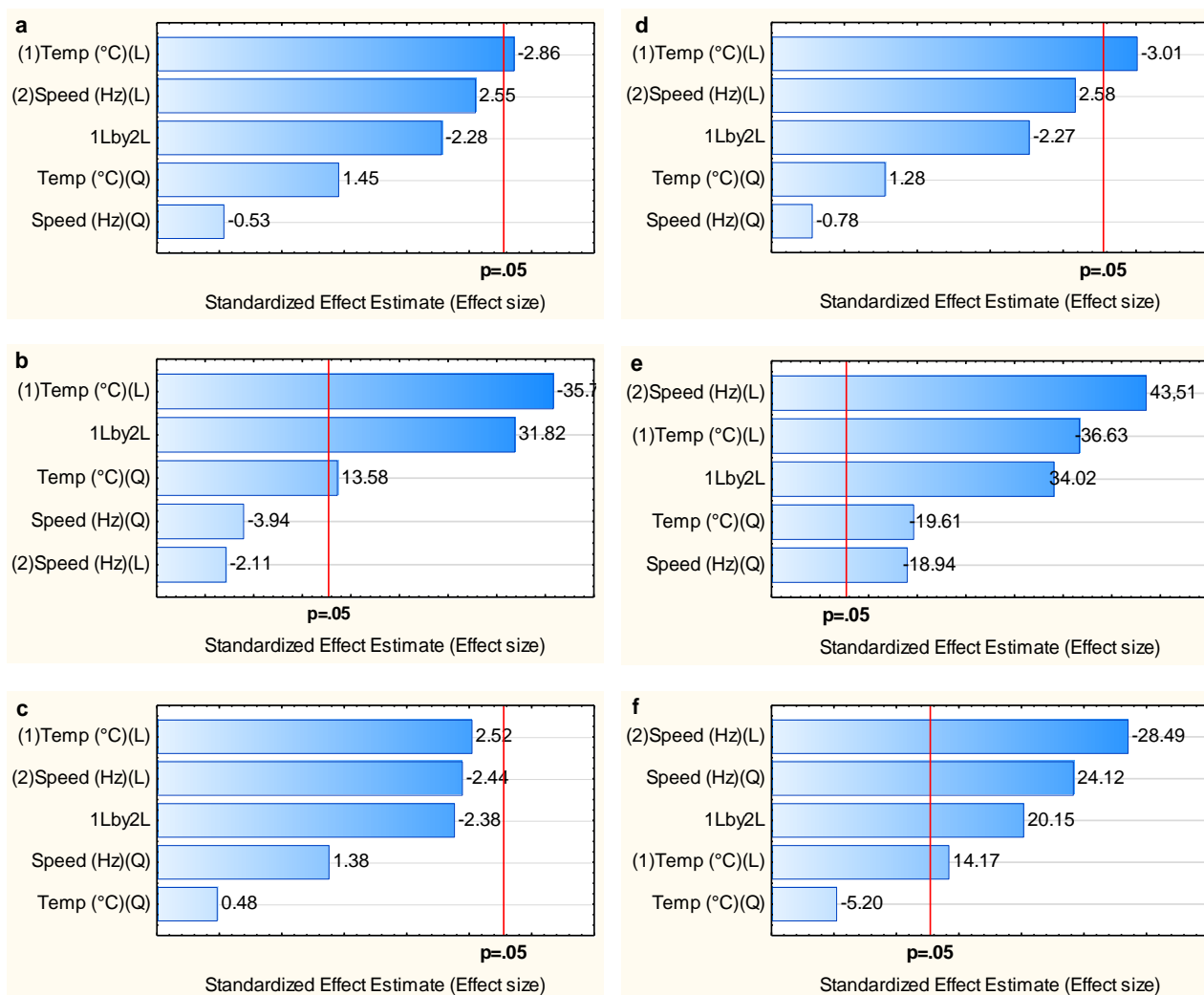
Figure 4.2. Pareto charts of standardised effect estimates (p =0.05) of (a) moisture content, (b) total essential amino acids [TEAA] and (c) yellowness index [YI] for H2G1 and (d) moisture content, (e) whiteness index [WI] and (f) total amino acids [TAA] for H7D1 at varying roasting temperatures and speeds (crossing the vertical red line by a bar at p =0.05 indicated significant effect otherwise not significant).

Total phenolics and flavonoids and DPPH antioxidant activity

Total phenolics content of the roasted H2G1 and H7D1 ranged from 1.78 to 2.09 and 1.34 to 1.67 g GAE/100g, total flavonoids from 0.30 to 0.39 and 0.24 to 0.32 mg CE/g, and DPPH antioxidant activity from 736.15 to 890.95 and 678.54 to 766.25 mM AAE/g, respectively (Table 4.1). The prediction models of total phenolics, total flavonoids and DPPH antioxidant activity of H2G1 and H7D1 had R^2-values of 0.46 and 0.43, 0.44 and 0.65, and 0.42 and 0.62, respectively (Table 4.2). Linear effects of temperature and speed as well as the interaction effect on the total phenolics content of H2G1 were significant (p ≤0.05) with positive effect sizes whereas those of H7D1 were not (p >0.05). This indicated that the total phenolics content of H2G1 significantly increased with increase in roasting temperature and rotating speed while variation in temperature and speed did

not significantly change that of H7D1. The antioxidant content and activity of some foods significantly increased during dry heat roasting due to production of new compounds with phenolics-like structures such as melanoidins by Maillard reaction (Lemos *et al.*, 2012) which could be responsible for the increase in total phenolics content of H2G1. Total flavonoids content and DPPH antioxidant activity of both hybrids did not significantly change with variation in roasting temperature and rotating speed (Table 4.2). Boiled, steamed and microwave roasted pumpkins and leeks did not show significant change in DPPH antioxidant activity (Turkmen *et al.*, 2005). The phenolic compounds such as phenolic acids and flavonoids found in cereal grains are concentrated in the bran, therefore consumption of whole cereal grains are recommended compared to refined cereal grains for health benefit (Adom & Liu, 2002). Epidemiological studies have shown that consumption of whole cereal grains reduces certain types of cancers and coronary heart diseases (Rice-Evans *et al.*, 1997). Therefore, in addition to providing energy, minerals and vitamins, the whole grain meal of H2G1 and H7D1 would provide health benefits to human consumers.

Optimisation of roasting conditions

The optimisation of roasting conditions was achieved using desirability profiling where the overall desirability function (D) was obtained by assigning predicted values a score ranging from 0 (very undesirable) to 1 (very desirable) specified from individual desirability functions (d_i) of each response variable (Bezerra *et al.*, 2008). Desirability profile indicates the level of process variables that produced the most desirable predicted response variables. Response variables can be maximised, minimised or held constant (maintained) during desirability profiling. Prediction model that fits experimental data very well should have R^2 ≥0.8 and a non-significant (p >0.05) lack-of-fit (Guan & Yao, 2008). The moisture content of both hybrids, YI and TEAA of H2G1, and WI and TAA of H7D1 with R^2-values between 0.82 and 0.90 and non-significant lack-of-fit (Table 4.3) were used for the optimisation process. Moisture content of ≤13.5% was maintained (Humpf & Voss, 2004) to obtain optimum conditions (roasting temperature and rotating speed) to minimise YI and maximise WI, TEAA and TAA in the desirability profiles. Roasting conditions of 234.0 °C; 90.0 Hz and 136.0 °C; 41.0 Hz (Fig. 3) were found to obtain minimum YI and maximum TEAA, respectively of H2G1 whole grain meal (Fig. 4.4). Average of the roasting temperatures (185.0 °C) and speeds (65.5 Hz) would therefore be considered as mean optimum roasting condition for H2G1 hybrid. Similarly, 204.6 °C; 90.0 Hz and 160.5 °C; 20.0 Hz (Fig. 4.3) were found to be the optimum roasting conditions to produce H7D1 whole grain meal (Fig. 4.4) with maximum WI and TAA, respectively. Therefore, the mean optimum roasting condition of H7D1 hybrid would be 182.6 °C/55.0 Hz.

Table 4.1. Roasting temperatures, rotating speeds of experimental runs generated using a central composite design and average values of the response variables of roasted H2G1 and H7D1 maize hybrids

Experimental run	Moisture (%)	BD (g/cm³)	WI meal	YI meal	pH	C/F ratio	Protein (%)	TAA (g/100 g)	TEAA (g/100 g)	TP (g GAE/100g)	TF (mg CE/g)	DPPH (mM AAE/g)
H2G1												
136°C/55Hz	14.64	0.71	85.43	17.26	6.16	2.33	8.04	6.26	2.82	1.95	0.38	862.57
150°C/30Hz	10.62	0.69	85.30	17.60	6.14	2.37	8.07	6.44	2.89	1.98	0.39	808.39
150°C/80Hz	14.23	0.72	85.40	17.54	6.17	2.45	8.01	5.80	2.56	1.78	0.30	736.15
185°C/20Hz	11.08	0.66	83.37	20.81	6.07	2.76	8.01	4.95	2.53	1.80	0.36	849.67
185°C/55Hz(C)	11.84	0.71	85.73	17.30	6.27	2.78	8.24	5.92	2.61	1.94	0.35	870.31
185°C/55Hz(C)	11.90	0.68	84.69	18.61	6.14	2.73	8.11	5.90	2.60	1.95	0.38	821.29
185°C/90Hz	12.14	0.69	84.93	18.34	6.16	2.52	8.04	5.96	2.65	2.08	0.39	890.95
220°C/30Hz	11.65	0.57	79.34	26.35	6.13	3.17	8.13	5.61	2.47	2.03	0.39	756.79
220°C/80Hz	11.88	0.68	83.66	18.24	6.11	2.38	8.07	5.88	2.59	2.09	0.38	820.43
234°C/55Hz	11.32	0.64	84.33	19.08	6.13	2.14	7.96	5.87	2.59	1.96	0.37	778.29
H7D1												
136°C/55Hz	14.55	0.72	85.40	17.57	6.32	2.36	8.01	5.68	2.53	1.46	0.28	706.05
150°C/30Hz	10.72	0.69	86.88	15.99	6.24	2.85	8.26	5.95	2.62	1.38	0.24	679.40
150°C/80Hz	14.64	0.72	85.86	17.07	6.28	2.65	8.11	5.35	2.38	1.46	0.29	694.87
185°C/20Hz	11.28	0.61	82.60	22.16	6.09	2.86	8.13	6.30	3.83	1.42	0.30	730.13
185°C/55Hz(C)	12.58	0.68	86.16	17.12	6.17	2.92	8.17	5.70	2.55	1.41	0.29	728.41
185°C/55Hz(C)	11.46	0.69	86.07	17.06	6.22	2.47	7.83	5.72	2.53	1.34	0.28	678.54
185°C/90Hz	12.30	0.71	86.53	16.47	6.24	3.21	8.26	5.94	2.66	1.41	0.28	766.25
220°C/30Hz	10.94	0.58	82.66	21.91	6.16	3.32	8.08	5.87	2.57	1.34	0.29	741.31
220°C/80Hz	11.30	0.67	85.97	17.08	6.18	2.61	8.04	5.84	2.62	1.38	0.27	733.57
234°C/55Hz	12.03	0.62	83.65	20.68	6.21	2.78	7.98	5.79	2.57	1.67	0.32	746.47

C= center point, BD = bulk density, WI = whiteness index, YI = yellowness index, C/F = coarse/fine, TAA = total amino acids, TEAA = total essential amino acids, TP = total phenolics, TF = total flavonoids, DPPH = 2,2-diphenyl-1-picrylhydrazyl antioxidant activity

Table 4.2. Effect size and corresponding p and R^2 values of the response variables of roasted H2G1 and H7D1 maize hybrids

Response variable	Effect	Effect size		p-value		R^2	
		H2G1	H7D1	H2G1	H7D1	H2G1	H7D1
Bulk density	TL	-3.87	-17.33	0.02	0.00	0.87	0.99
	SL	2.73	15.02	0.05	0.00		
	TQ	-1.14	-2.59	0.32	0.06		
	SQ	-1.14	-4.34	0.32	0.01		
	IL	1.69	4.88	0.17	0.01		
pH	TL	-1.55	-3.22	0.20	0.03	0.69	0.87
	SL	1.92	2.84	0.13	0.05		
	TQ	0.13	1.99	0.91	0.12		
	SQ	-1.26	-0.88	0.28	0.43		
	IL	-0.86	-0.30	0.44	0.78		
C/F ratio	TL	8.46	1.14	0.08	0.46	0.87	0.57
	SL	-10.51	-0.47	0.06	0.72		
	TQ	-10.26	-0.33	0.06	0.80		
	SQ	-2.04	1.24	0.29	0.43		
	IL	-12.30	-0.80	0.05	0.57		
Protein	TL	0.07	-0.74	0.95	0.50	0.52	0.47
	SL	-0.34	0.00	0.75	1.00		
	TQ	-1.86	0.07	0.14	0.95		
	SQ	-1.57	1.55	0.19	0.20		
	IL	-0.05	0.42	0.96	0.70		
TAA[#]	TL	-32.56	6.18	0.02	0.10	0.67	0.65
TEAA[$]	SL	26.23	-45.93	0.02	0.01		
	TQ	18.75	-13.38	0.03	0.05		
	SQ	-27.70	39.55	0.02	0.02		
	IL	32.17	10.25	0.02	0.06		
WI[#]	TL	-2.32	3.06	0.08	0.04	0.75	0.88
YI[$]	SL	1.65	-3.48	0.17	0.03		
	TQ	-0.68	1.25	0.54	0.28		
	SQ	-1.23	1.42	0.29	0.23		
	IL	1.49	-2.47	0.21	0.07		
Total Phenolics	TL	39.08	1.17	0.02	0.45	0.46	0.43
	SL	26.71	0.76	0.02	0.59		
	TQ	6.56	2.84	0.10	0.22		
	SQ	0.92	-0.32	0.53	0.80		
	IL	36.77	-0.41	0.02	0.74		
Total flavonoids	TL	1.40	2.41	0.40	0.25	0.44	0.65
	SL	-1.38	0.05	0.40	0.97		
	TQ	0.38	0.31	0.77	0.81		
	SQ	0.32	-0.53	0.80	0.69		
	IL	2.23	-2.71	0.27	0.23		
DPPH	TL	-0.88	1.58	0.45	0.36	0.42	0.62
	SL	0.50	0.59	0.70	0.66		
	TQ	-1.84	0.29	0.32	0.82		
	SQ	-0.29	0.96	0.82	0.51		
	IL	1.96	-0.33	0.30	0.80		

R^2 = coefficient of determination, TL = temperature linear effect, SL = speed linear effect, TQ = temperature quadratic effect, SQ = speed quadratic effect, IL = interaction linear effect, YI = yellowness index, TEAA = total essential amino acids, [#]TAA and [#]WI of [#]H2G1, [$]YI and [$]TEAA of H7D1

Table 4.3. Regression coefficients (R^2) and p values of lack-of-fit for moisture content, whiteness index (WI) and yellowness index (YI) of roasted H2G1 and H7D1 maize hybrids

Response variable	Effect	Regression coefficient		R^2		p-value of Lack-of-fit	
		H2G1	H7D1	H2G1	H7D1	H2G1	H7D1
Moisture	Mean	17.91894	16.41551				
	$\beta_1 X_1$	-0.12276	-0.11165	0.86	0.86	0.23	0.09
	$\beta_2 X_2$	0.23863	0.26801				
	$\beta_{11} X_1^2$	0.00042	0.00039				
	$\beta_{22} X_2^2$	-0.00030	-0.00046				
	$\beta_{12} X_1 X_2$	-0.00097	-0.00102				
TEAA[#]	Mean	5.60753	7.11854	0.87	0.86	0.07	0.07
TAA[$]	$\beta_1 X_1$	-0.02338	0.00360				
	$\beta_2 X_2$	-0.02168	-0.06430				
	$\beta_{11} X_1^2$	0.00004	-0.00003				
	$\beta_{22} X_2^2$	-0.00002	0.00026				
	$\beta_{12} X_1 X_2$	0.00013	0.00001				
YI[#]	Mean	5.86930	81.61741	0.83	0.87	0.34	0.06
WI[$]	$\beta_1 X_1$	0.05326	0.08688				
	$\beta_2 X_2$	0.17271	-0.08904				
	$\beta_{11} X_1^2$	0.00032	-0.00048				
	$\beta_{22} X_2^2$	0.00176	-0.00091				
	$\beta_{12} X_1 X_2$	-0.00169	0.00124				

β = regression coefficient, X_1 = temperature linear effect, X_2 = speed linear effect, $X_1 X_2$ = interaction linear effect, X_1^2 = temperature quadratic effect, X_2^2 = speed quadratic effect, R^2 = coefficient of determination, TEAA = total essential amino acids, TAA = total amino acids, WI = whiteness index, [#]TEAA and [#]YI of H2G1, [$]TAA and [$]WI of H7D1
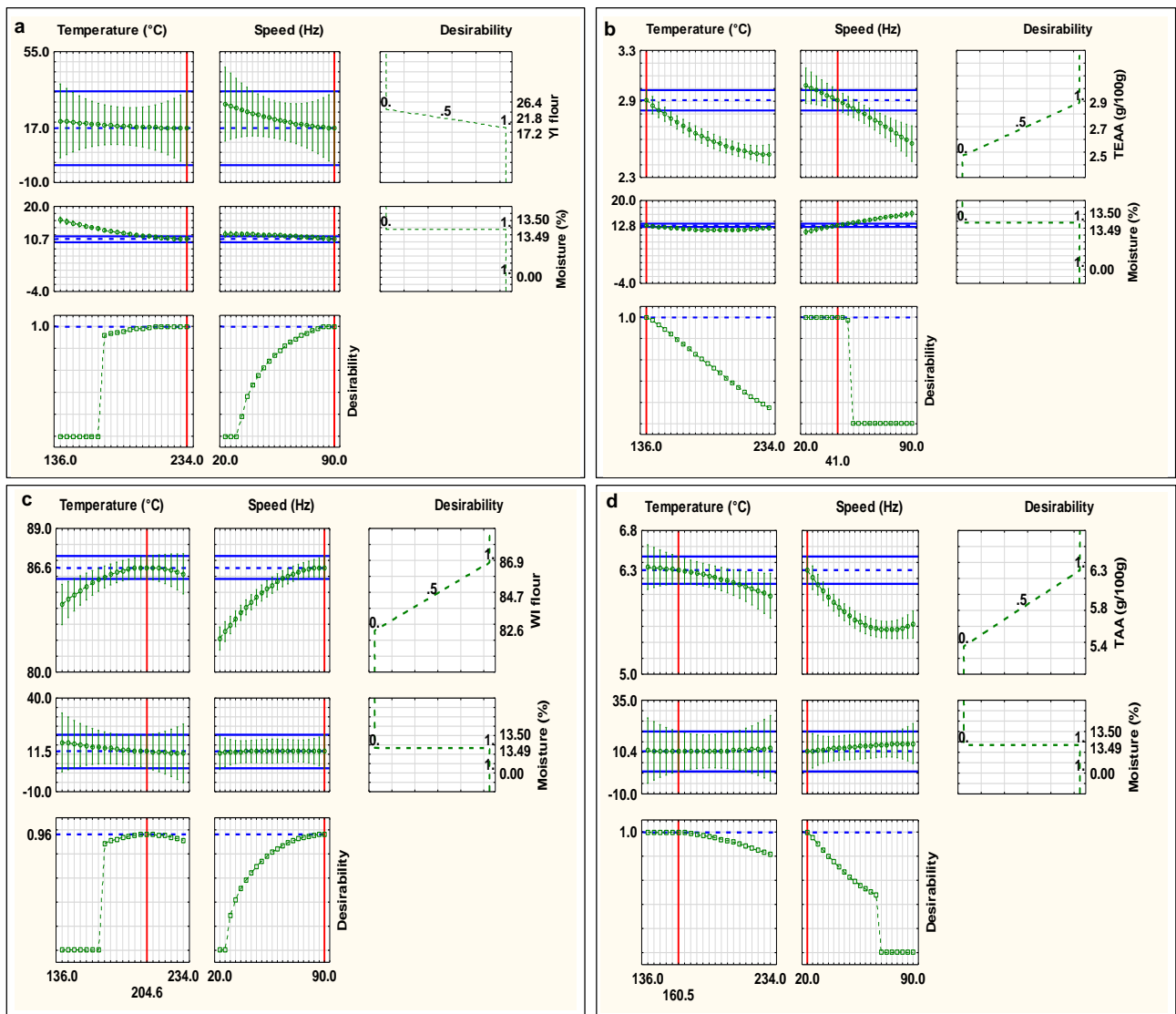
Figure 4.3. Desirability profiles at moisture content (≤13.50%) of (a) yellowness index [YI], (b) total essential amino acids [TEAA] of whole grain meal for the optimisation of roasting conditions of H2G1 and (c) whiteness index [WI], (d) total amino acids [TAA] of whole grain meal for the optimisation of roasting conditions of H7D1 (horizontal continuous blue lines in the graphs indicate confidence intervals used and the intersection of the horizontal dotted blue and vertical continuous red lines indicate the optimum roasting conditions).
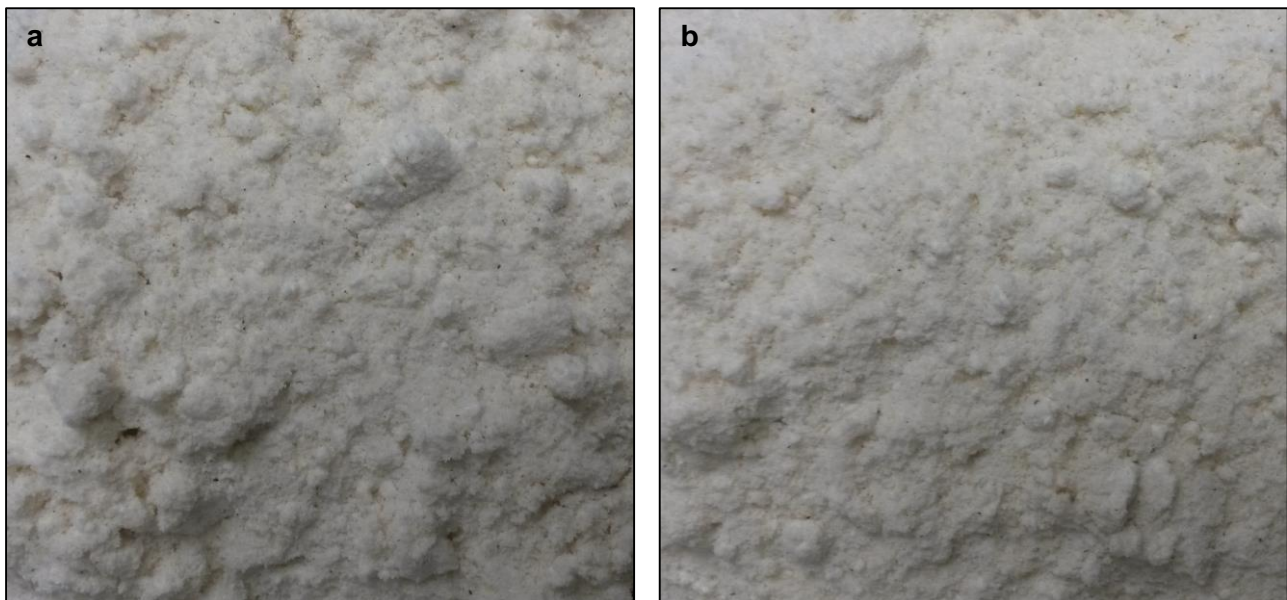
Figure 4.4. Whole grain meal of the roasted (a) H2G1 and (b) H7D1 produced using the mean optimum roasting conditions 185.0 °C/65.5 Hz and 182.6 °C/55.0 Hz, respectively.

Conclusion

Kernel hardness, protein content, total flavonoids and DPPH antioxidant activity of the two maize hybrids studied were not significantly affected by variation in roasting temperature and rotating speed in the range investigated. The bulk density of both hybrids, TAA and total phenolics of H2G1, and pH, YI and WI of H7D1 were significantly affected by changes in temperature and speed of roasting. Increase in temperature significantly decreased the moisture content of both hybrids and TEAA of H2G1, whereas decrease in rotating speed significantly increased the TEAA and TAA of H7D1. This study showed that to produce whole grain meal of H2G1 and H7D1 maize hybrids with the best quality and nutritional value, the mean optimum roasting conditions 185.0 °C/65.5 Hz and 182.6 °C/55.0 Hz, respectively should be used.

References

AACC (1999). *Approved methods of the american association of cereal chemists international.* St. Paul, Minnesota, USA: AACC International.

Adom, K.K. & Liu, R.H. (2002). Antioxidant activity of grains. *Journal of Agricultural and Food Chemistry,* **50,** 6182-6187.

Batterham, E., Lowe, R., Darnell, R. & Major, E. (1986). Availability of lysine in meat meal, meat and bone meal and blood meal as determined by the slope-ratio assay with growing pigs, rats and chicks and by chemical techniques. *British Journal of Nutrition,* **55,** 427-440.

Bezerra, M.A., Santelli, R.E., Oliveira, E.P., Villar, L.S. & Escaleira, L.A. (2008). Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta,* **76,** 965-977.

Blandino, M., Mancini, M.C., Peila, A., Rolle, L., Vanara, F. & Reyneri, A. (2010). Determination of maize kernel hardness: Comparison of different laboratory tests to predict dry-milling performance. *Journal of the Science of Food and Agriculture,* **90,** 1870-1878.

CAF (2014). Total amino acids content of hydrolysed samples. Stellenbosch University, South Africa. URL: http://academic.sun.ac.za/saf/services/services1.html Accessed 25/March/2014.

Cämmerer, B. & Kroh, L.W. (2009). Shelf life of linseeds and peanuts in relation to roasting. *LWT - Food Science and Technology,* **42,** 545-549.

Chung, H.-S., Chung, S.-K. & Youn, K.-S. (2011). Effects of roasting temperature and time on bulk density, soluble solids, browning index and phenolic compounds of corn kernels. *Journal of Food Processing and Preservation,* **35,** 832-839.

Craig, W.M. & Broderick, G.A. (1981). Effect of heat treatment on true digestibility in the rat, in vitro proteolysis and available lysine content of cottonseed meal protein. *Journal of Animal Science,* **52,** 292-301.

De Munter, J.S., Hu, F.B., Spiegelman, D., Franz, M. & Van Dam, R.M. (2007). Whole grain, bran, and germ intake and risk of type 2 diabetes: A prospective cohort study and systematic review. *PLoS Medicine,* **4,** 1385-1395.

FDA (2015). pH values of various foods. U. S. Food and Drug Administration. New Hampshire, MD, USA. URL: http://www.fda.gov/Food/FoodborneIllnessContaminants/CausesOfIllnessBadBugBook/ucm 122561.htm Accessed 3/December/2014.

Fritz, T. (2013). Backgound and working principle (operation manual) of forced convection continuous tumble roaster (FCCTR). Bloemfontein, South Africa: Roastech.

Good, C.K., Holschuh, N., Albertson, A.M. & Eldridge, A.L. (2008). Whole grain consumption and body mass index in adult women: An analysis of nhanes 1999-2000 and the USDA pyramid servings database. *Journal of the American College of Nutrition,* **27,** 80-87.

Guan, X. & Yao, H. (2008). Optimization of viscozyme L-assisted extraction of oat bran protein using response surface methodology. *Food Chemistry,* **106,** 345-351.

Hefnawy, T.H. (2011). Effect of processing methods on nutritional composition and anti-nutritional factors in lentils (*Lens culinaris*). *Annals of Agricultural Sciences,* **56,** 57-61.

Hernandez, J., Heyd, B., Irles, C., Valdovinos, B. & Trystram, G. (2007). Analysis of the heat and mass transfer during coffee batch roasting. *Journal of Food Engineering,* **78,** 1141-1148.

Hoseney, R.C. (1994). *Principles of cereal science and technology.* St. Paul, Minnesota, USA: American Association of Cereal Chemists (AACC).

Humpf, H.-U. & Voss, K.A. (2004). Effects of thermal food processing on the chemical structure and toxicity of fumonisin mycotoxins. *Molecular Nutrition and Food Research,* **48,** 255-269.

Jensen, M.K., Koh-Banerjee, P., Hu, F.B., Franz, M., Sampson, L., Grønbæk, M. & Rimm, E.B. (2004). Intakes of whole grains, bran, and germ and the risk of coronary heart disease in men. *The American Journal of Clinical Nutrition,* **80,** 1492-1499.

Jha, S.N. (2005). Mathematical simulation of roasting of grain. *Journal of Food Engineering,* **71,** 304-310.

Kahyaoglu, T. (2008). Optimization of the pistachio nut roasting process using response surface methodology and gene expression programming. *LWT - Food Science and Technology,* **41,** 26-33.

Karioti, A., Hadjipavlou-Litina, D., Mensah, M.L., Fleischer, T.C. & Skaltsa, H. (2004). Composition and antioxidant activity of the essential oils of *Xylopia aethiopica* (Dun) A. Rich. (Annonaceae) leaves, stem bark, root bark, and fresh and dried fruits, growing in Ghana. *Journal of Agricultural and Food Chemistry,* **52,** 8094-8098.

Kayitesi, E., De Kock, H.L., Minnaar, A. & Duodu, K.G. (2012). Nutritional quality and antioxidant activity of marama–sorghum composite flours and porridges. *Food Chemistry,* **131,** 837-842.

Kennedy, J.F. & Knill, C.J. (2003). Food colloids: Fundamentals of formulation: E. Dickinson, R. Miller (Eds.); the royal society of chemistry, cambridge. *Carbohydrate Polymers,* **51,** 361.

Lee, K.-M., Herrman, T.J., Lingenfelser, J. & Jackson, D.S. (2005). Classification and prediction of maize hardness-associated properties using multivariate statistical analyses. *Journal of Cereal Science,* **41,** 85-93.

Lee, S. & Lee, J. (2009). Effects of oven-drying, roasting, and explosive puffing process on isoflavone distributions in soybeans. *Food Chemistry,* **112,** 316-320.

Lemos, M.R.B., Siqueira, E.M.D.A., Arruda, S.F. & Zambiazi, R.C. (2012). The effect of roasting on the phenolic compounds and antioxidant potential of baru nuts [*Dipteryx alata* Vog.]. *Food Research International,* **48,** 592-597.

Maruatona, G.N., Duodu, K.G. & Minnaar, A. (2010). Physicochemical, nutritional and functional properties of marama bean flour. *Food Chemistry,* **121,** 400-405.

Mcnaughton, J. & Reece, F. (1980). Effect of moisture content and cooking time on soybean meal urease index, trypsin inhibitor content, and broiler growth. *Poultry Science,* **59,** 2300-2306.

Mcniven, M.A., Hamilton, R.M.G., Robinson, P.H. & Deleeuw, J.W. (1994). Effect of flame roasting on the nutritional quality of common cereal grains for non-ruminants and ruminants. *Animal Feed Science and Technology,* **47,** 31-40.

Mendes, L.C., De Menezes, H.C., Aparecida, M. & Da Silva, A. (2001). Optimization of the roasting of robusta coffee (*C. canephora* Conillon) using acceptability tests and RSM. *Food Quality and Preference,* **12,** 153-162.

Milán-Carrillo, J., Gutiérrez-Dorado, R., Cuevas-Rodríguez, E., Garzón-Tiznado, J. & Reyes-Moreno, C. (2004). Nixtamalized flour from quality protein maize (*Zea mays* L.). Optimization of alkaline processing. *Plant Foods for Human Nutrition,* **59,** 35-44.

Murthy, K.V., Ravi, R., Bhat, K.K. & Raghavarao, K.S.M.S. (2008). Studies on roasting of wheat using fluidized bed roaster. *Journal of Food Engineering,* **89,** 336-342.

Nursten, H.E. (2005). *The maillard reaction: Chemistry, Biochemistry, and implications.* Cambridge, UK: Royal Society of Chemistry.

Nyembwe, P., Minnaar, A., Duodu, K.G. & De Kock, H.L. (2015). Sensory and physicochemical analyses of roasted marama beans [*Tylosema esculentum* (Burchell) A. Schreiber] with specific focus on compounds that may contribute to bitterness. *Food Chemistry,* **178,** 45-51.

O'kennedy, K. (2011). *Characterisation of zein from south african maize of varying endosperm texture.* MSc Thesis, Stellenbosch University.

O'neil, C.E., Nicklas, T.A., Zanovec, M. & Cho, S. (2010). Whole-grain consumption is associated with diet quality and nutrient intake in adults: The national health and nutrition examination survey, 1999-2004. *Journal of the American Dietetic Association,* **110,** 1461-1468.

Oliviero, T., Capuano, E., CäMmerer, B. & Fogliano, V. (2008). Influence of roasting on the antioxidant activity and hmf formation of a cocoa bean model systems. *Journal of Agricultural and Food Chemistry,* **57,** 147-152.

Özdemir, M., Açkurt, F., Yildiz, M., Biringen, G., Gürcan, T. & Löker, M. (2001). Effect of roasting on some nutrients of hazelnuts (*Corylus avellena* L.). *Food Chemistry,* **73,** 185-190.

Park, M., Kim, K. & Kim, J. (1993). Changes in the physicochemical properties of ginseng by roasting. *Journal of Ginseng Research,* **17,** 228-231.

Pathare, P.B., Opara, U.L. & Al-Said, F.a.-J. (2013). Colour measurement and analysis in fresh and processed foods: A review. *Food and Bioprocess Technology,* **6,** 36-60.

Reyes-Moreno, C., Milán-Carrillo, J., Gutiérrez-Dorado, R., Paredes-López, O., Cuevas-Rodrıguez, E. & Garzón-Tiznado, J. (2003). Instant flour from quality protein maize (*Zea mays* L.). Optimization of extrusion process. *LWT-Food Science and Technology,* **36,** 685-695.

Rice-Evans, C., Miller, N. & Paganga, G. (1997). Antioxidant properties of phenolic compounds. *Trends in Plant Science,* **2,** 152-159.

Saklar, S., Ungan, S. & Katnas, S. (2003). Microstructural changes in hazelnuts during roasting. *Food Research International,* **36,** 19-23.

Schatzkin, A., Mouw, T., Park, Y., Subar, A.F., Kipnis, V., Hollenbeck, A., Leitzmann, M.F. & Thompson, F.E. (2007). Dietary fiber and whole-grain consumption in relation to colorectal cancer in the nih-aarp diet and health study. *The American Journal of Clinical Nutrition,* **85,** 1353-1360.

Sriperm, N., Pesti, G.M. & Tillman, P.B. (2011). Evaluation of the fixed nitrogen-to-protein (N: P) conversion factor (6.25) versus ingredient specific N: P conversion factors in feedstuffs. *Journal of the Science of Food and Agriculture,* **91,** 1182-1186.

Steffen, L.M., Jacobs, D.R., Stevens, J., Shahar, E., Carithers, T. & Folsom, A.R. (2003). Associations of whole-grain, refined-grain, and fruit and vegetable consumption with risks of all-cause mortality and incident coronary artery disease and ischemic stroke: The atherosclerosis risk in communities (ARIC) study. *The American Journal of Clinical Nutrition,* **78,** 383-390.

Turkmen, N., Sari, F. & Velioglu, Y.S. (2005). The effect of cooking methods on total phenolics and antioxidant activity of selected green vegetables. *Food Chemistry,* **93,** 713-718.

Ufaz, S. & Galili, G. (2008). Improving the content of essential amino acids in crop plants: Goals and opportunities. *Plant Physiology,* **147,** 954-61.

USDA (2015). Corn production by country in 1000MT. United States Department of Agriculture. URL: http://www.indexmundi.com/agriculture/?commodity=corn Accessed 21/February/2015.

Waigh, T.A., Gidley, M.J., Komanshek, B.U. & Donald, A.M. (2000). The phase transformations in starch during gelatinisation: A liquid crystalline approach. *Carbohydrate Research,* **328,** 165-176.

Wang, L., Chen, J., Xie, H., Ju, X. & Liu, R.H. (2013). Phytochemical profiles and antioxidant activity of adlay varieties. *Journal of Agricultural and Food Chemistry,* **61,** 5103-5113.

Yang, J., Martinson, T.E. & Liu, R.H. (2009). Phytochemical profiles and antioxidant activities of wine grapes. *Food Chemistry,* **116,** 332-339.

Yazdanpanah, H., Mohammadi, T., Abouhossain, G. & Cheraghali, A.M. (2005). Effect of roasting on degradation of aflatoxins in contaminated pistachio nuts. *Food and Chemical Toxicology,* **43,** 1135-1139.

Youn, K.-S. & Chung, H.-S. (2012). Optimization of the roasting temperature and time for preparation of coffee-like maize beverage using the response surface methodology. *LWT - Food Science and Technology,* **46,** 305-310.

Žilić, S., Serpen, A., Akıllıoğlu, G., Gökmen, V. & Vančetović, J. (2012). Phenolic compounds, carotenoids, anthocyanins, and antioxidant capacity of colored maize (*Zea mays* L.) kernels. *Journal of Agricultural and Food Chemistry,* **60,** 1224-1231.

CHAPTER FIVE

Chapter 5

Proximate composition, antioxidant and pasting properties of raw, roasted whole grain and unroasted refined commercial maize (*Zea mays* L.) flours

Abstract

Proximate composition, antioxidant and pasting properties of whole grain flours of raw and roasted Nigerian (S28, S33) and South African (H2G1, H7D1) maize varieties were studied in comparison to a refined commercial maize meal (CMM). Forced convection roasting was conducted using the mean optimum roasting conditions (roasting temperature/rotating speed) 189.9 ºC/90.0 Hz, 140.9 ºC/49.8 Hz, 185.0 ºC/65.5 Hz and 182.6 ºC/55.0 Hz for S28, S33, H2G1 and H7D1, respectively. There was no significant change in crude protein, crude oil, ash and crude fiber of the whole grain flours of the unroasted and roasted maize varieties and the carbohydrate content significantly decreased. The protein, oil, ash and fiber of the unroasted and roasted whole grain flours were significantly higher than those of CMM. However, carbohydrate content of the later was significantly higher than that of the whole grain flours. Total phenolics content of the maize varieties did not differ significantly after roasting, except that of H2G1 which showed significant increase. There was no significant change in total flavonoids, DPPH and ABTS antioxidant activity between the unroasted and roasted whole grain flours. The total phenolics and flavonoids content, DPPH and ABTS radical scavenging activity of the whole grain flours were significantly higher than those of CMM. Whole grain flour of the roasted maize had significantly higher pasting viscosities (peak, final, breakdown, trough and setback) than the unroasted. There was no significant change in pasting temperatures between the unroasted and roasted maize whole grain flours. The non-significant change in protein, oil, ash and fiber content, antioxidant activity, pasting temperatures, and significantly higher pasting viscosities of whole grain flours of the roasted than the unroasted maize varieties indicated the effectiveness of FCR. The high content of protein, oil, fiber, ash, phenolics and flavonoids as well as antioxidant activity of the whole grain flours demonstrated superior nutritional quality compared to CMM.

Introduction

Maize flour and meal are the most popular intermediate products of maize and staple food in many parts of developing countries such as Nigeria, South Africa and Mexico. Maize flour and meal can be processed into different types of end products for human consumption (Ranum *et al.*, 2014). Maize and its products are important sources of macronutrients (carbohydrate, protein and fat), micronutrients (vitamins and minerals) and phytochemicals such as phenolic acids, lignans and flavonoids (Oboh *et al.*, 2010). The phytochemicals and micronutrients are predominantly concentrated in the outer layer (bran) and germ of the maize kernel. During the production of flour or meal, the bran and germ are usually removed and fed to animals. The health benefits of bran and germ in whole grain food products were reported. Consumption of whole grain cereals was found to be associated with reduction in weight due to decrease in energy intake (Melanson *et al.*, 2006; Katcher *et al.*, 2008; Maki *et al.*, 2010). In addition it led to reduced instances of colorectal cancer (Schatzkin *et al.*, 2007; Aune *et al.*, 2011), coronary heart diseases (Jensen *et al.*, 2004; Mellen *et al.*, 2008; Nettleton *et al.*, 2008; Harris & Kris-Etherton, 2010), type 2 diabetes mellitus (de Munter *et al.*, 2007) and hypertension (Behall *et al.*, 2006; Wang *et al.*, 2007).

Extraction rate is the proportion of flour or meal obtained from the whole grain maize after dry milling. The extraction rate of maize varies among countries worldwide depending on the product, which is usually between 60 and 100%. For instance, the extraction rate for yellow maize products in USA is in the range of 60 to 65%. In African countries such as Nigeria and South Africa white maize is mostly consumed and the extraction rates are generally higher, ranging from 62 to 99%. Products with extraction rate of 62% are known as super, while those with 79 - 89% are called sifted, and fractions having 99% are referred to as unsifted (NCM, 2015). In Africa, maize consumption ranges between 52 (Uganda) and 328 (Lesotho) g/person/day. While in the Americas, it was estimated to be between 50 (Haiti) and 267 (Mexico) g/person/day. These regions have the highest maize consumption in the world with estimated average consumption of >50 g/person/day and average extraction rate of 80% (Ranum *et al.*, 2014). Consumption of whole grain flour or meal of maize should be encouraged due to the health benefits associated with it. Usually, the production of intermediate and ready to eat maize food products requires heating.

Heat-processing is the conversion of raw food substances into intermediate and ready to eat food products using heat. In the presence of moisture, heat-processing induced absorption of water, loss of crystallinity and subsequent swelling of starch granules resulting to amylose leaching (Jenkins & Donald, 1998). Heat-processing (roasting, nixtamalisation, extrusion, boiling, baking or microwaving) under optimum conditions enhances the colour, texture, flavour and nutritional qualities of food products. Carbohydrate, crude oil, crude protein, crude fiber and ash content did not significantly differ between raw and roasted whole grains of maize (Ayatse *et al.*, 1983). Dry heat roasting significantly increased the antioxidants content and activity of maize grains (Chung *et al.*, 2011; Youn & Chung, 2012) and soybeans (Lee & Lee, 2009). Dry heat roasting of maize results in significant decrease in extractible phenolics, flavonoids content and DPPH radical scavenging ability,

and increased ferric reducing power (Oboh *et al.*, 2010). However, it was reported that forced convection roasting of Nigerian maize cultivars using superheated steam (dry steam) did not cause significant changes in pH, kernel hardness, crude protein, amino acids profile, total phenolics, flavonoids and DPPH antioxidant activity (Chapter 3). Forced convection roasted (using superheated steam) South African maize hybrids showed non-significant effect on kernel hardness, total flavonoids and antioxidant activity (Chapter 4). There was a decrease in pasting viscosities and an increase in gelatinisation temperatures of starch of maize grains heated at 100 °C and 30% moisture for 16 h (Hoover & Manuel, 1996). Similarly, Stevenson *et al.* (2005) reported that all the pasting viscosity parameters of microwaved maize starch (15 – 40% moisture content) decreased while the pasting temperature increased. The aim of this study was to compare the proximate composition, antioxidant and pasting properties of raw and roasted whole grain maize flours with those of an unroasted refined commercial maize meal.

Materials and methods

Material

Four maize samples (5 kg each) from Nigeria and South Africa were used for the experiments (Table 5.1). Nigerian maize cultivars (S28 and S33) were obtained from the Institute for Agricultural Research, Ahmadu Bello University (Samaru, Zaria) and the South African maize hybrids (H2G1 and H7D1) were kindly provided by PANNAR Seeds (Greytown, KwaZulu-Natal). Uninfected maize samples of uniform kernel size were cleaned by removing foreign materials and broken kernels. Refined commercial maize meal (bran and germ removed during processing) was purchased from supermarkets in Stellenbosch, Western Cape, South Africa and milled with a Cyclone Laboratory Mill, model 3100 (Perten Instruments, Hagersten, Sweden) using 0.8 mm sieve.

Table 5.1. Maize varieties, sources and properties

	Maize variety	Country	Source	Hardness	Colour
1	SAMMAZ 28 (S28)	Nigeria	Samaru, Zaria	Soft	Yellow
2	SAMMAZ 33 (S33)	Nigeria	Samaru, Zaria	Soft	White
3	H2G1	South Africa	Greytown, South Africa	Hard	White
4	H7D1	South Africa	Delmas, South Africa	Hard	White

Chemicals

Diethyl ether, sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), acetone, methanol, ethyl acetate, sodium carbonate (Na_2CO_3), sodium nitrite ($NaNO_2$), aluminium chloride ($AlCl_3$), sodium hydroxide (NaOH), potassium persulfate ($K_2O_8S_2$), sodium acetate trihydrate ($C_2H_3NaO_2 \cdot 3H_2O$), glacial acetate ($C_2H_4O_2$) and hydrochloric acid (HCl); Folin-Ciocalteau, DPPH (2,2-diphenyl-1-picrylhydrazyl) and ABTS [2,2′-Azino-bis(3-ethylbenzoline-6-sulfonic acid) diammonium salt]

reagents; and gallic acid and Catechin standards were purchased from Sigma-Aldrich (St. Louis, USA). Alfalfa (protein standard) was purchased from Leco Corporation (Leco Africa, Kempton Park, South Africa).

Tempering of maize kernels

Tempering was done to increase the moisture content of maize kernels to between 18 and 20% as required for the forced convection continuous tumble roaster (FCCTR). It was done according to the American Association of Cereal Chemists International (AACCI) Approved Method 26-95.01 (AACC, 1999) as described in Chapter 3.

Forced convection roasting

Cleaned, tempered maize kernels (200 g/run) were roasted in a FCCTR, model R100E (Roastech, Bloemfontein, South Africa) using the mean optimum roasting conditions (roasting temperature/rotating speed) 189.9 °C/90 Hz for S28, 140.9 °C/49.8 Hz for S33 (Chapter 3) and 185.0 °C/65.5 Hz for H2G1, 182.6 °C/55.0 Hz for H7D1 (Chapter 4). Ten replicates of roasting were performed for each of the four maize varieties. The roaster was operated at 150 °C, 20 Hz and tempered maize grains (2 kg of a different variety) were roasted in order to generate superheated steam which replaced dry hot-air in the roasting chamber of FCCTR. Then, roasting of the 200 g/run experimental samples were conducted. The roasted 200 g/run maize samples were allowed to cool to room temperature and milled using a Cyclone Laboratory Mill, model 3100 fitted with 0.8 mm sieve. Raw grains of the maize samples and refined commercial maize flour (CMM) were also milled. The flours obtained were stored in screw capped plastic containers at 4 °C prior to laboratory analyses.

Proximate composition

Crude protein was determined in duplicate by Dumas combustion method according to AACCI Approved Method 46–30.01 (AACC, 1999) using a Leco Instrument, model FP-528 (Leco Africa, Kempton Park, South Africa) as described in Chapter 3. Ash and moisture contents were determined in duplicate using standard methods as described in the AACCI Approved Methods 08-01.01 and 44-19.01, respectively (AACC, 1999). Crude fat (oil) was determined in duplicate using AOAC Official Method 920.39 (AOAC, 2002). Estimation of the content of crude protein and oil was carried out on dry matter basis. Total carbohydrate content (on dry matter basis) was estimated by difference using equation 1.

$$\text{Total carbohydrate } (\%) = 100 - (\text{crude protein} + \text{crude oil} + \text{ash} + \text{moisture}) \tag{1}$$

Determination of crude fiber

Crude fiber was determined in duplicate according to the AOAC Official Method 962.09 (AOAC, 2002). Maize flour (1 g) was weighed into a pre-dried glass crucible, 150 mL of preheated 0.128 M H_2SO_4 solution added and the mixture boiled under reflux for 30 min. The hot solution was quickly

filtered and the insoluble residue washed three times with hot distilled water to get rid of the acid. To the residue, 150 mL of hot 0.313 M NaOH solution was added and the mixture boiled again under reflux for 30 min. The solution was quickly filtered and the residue washed three times with hot distilled water to remove the base. The residue was rewashed three times with 20 mL acetone (to remove traces of water) and dried to a constant weight in an oven at 105 °C for 48 h. The crucible with its content was cooled in a desiccator for 30 min, weighed (C_1) and incinerated in a Muffle Furnace, model LEF-215P (Daihan Labtech, New Delhi, India) at 500 °C for 6 h. After cooling slowly to a temperature below 250 °C in the furnace, the crucible was transferred into a desiccator and cooled for 30 min, reweighed (C_2) and the fiber content calculated using equation 2.

$$\text{Crude fiber content (\%)} = \left(\frac{C_1 - C_2}{\text{Weight of maize flour}}\right) 100 \qquad (2)$$

Extraction of antioxidants

Bound and free phenolics were extracted according to the slightly modified method of Wang *et al.* (2013) as described in Chapter 3. The extracts were kept at -80 °C prior to analyses.

Determination of total phenolics

Total phenolics content was determined in duplicate using the Folin-Ciocalteau method (Žilić *et al.*, 2012). Standard and extract (100 µL each) was pipetted into labelled Eppendorf tube and 400 µL of distilled water added. The mixture was neutralised with 1.25 mL of 20% aqueous Na_2CO_3 and allowed to stand at room temperature for 40 min in the dark. Absorbance of the mixture was measured at 725 nm against a blank (absolute methanol) using a Helios Omega UV-vis spectrophotometer (Thermo scientific technologies, Madison, USA). Total phenolics content was expressed using gallic acid standard curve as milligram of gallic acid equivalent per gram of dry matter (mg GAE/g DM).

Determination of total flavonoids

Duplicate determination of total flavonoids content was done as described by Yang *et al.* (2009). The standard and extract (250 µL each) was pipetted into a centrifuge tube and 1.25 mL of distilled water added. A 5% $NaNO_2$ (75 µL) was added and the mixture shaken. This was allowed to stand at room temperature in the dark for 5 min and 150 µL of 10% $AlCl_3$ added. The mixture was shaken and kept in the dark for 6 min at room temperature. To the mixture, 500 µL of 1 M NaOH and 775 µL of distilled water were added and shaken. Absorbance of the mixture was measured at a wavelength of 510 nm using the Helios Omega UV-vis spectrophotometer. Total flavonoids content was expressed as milligram of catechin equivalent per gram of dry matter (mg CE/g DM) using catechin standard curve.

Determination of DPPH radical scavenging activity

The DPPH radical scavenging activity was determined in duplicate as described by Karioti *et al.* (2004) with minor modifications. Extract (20 µL each) was pipetted into Eppendorf tube and 980 µL of absolute methanol added. The mixture was shaken vigorously using a vortex, 1 mL of 0.1 mM DPPH methanolic solution added and kept in the dark at room temperature for 60 min. A control solution containing all the chemicals except the sample was used. Absorbance of the mixture was measured at 517 nm using the Helios Omega UV-vis spectrophotometer. Inhibition of the DPPH free radical by the extract was estimated as radical scavenging activity (RSA) using equation 3.

$$\text{DPPH RSA (\%)} = \left(\frac{A_C - A_E}{A_C}\right)100 \tag{3}$$

where A_E = absorbance of the reaction mixture containing extract, A_C = absorbance of control.

Determination of ABTS radical scavenging activity

Duplicate determination of ABTS radical scavenging activity was done according to the method of Thaipong *et al.* (2006) with some modifications. Stock solutions of 7.4 mM ABTS radical and 2.6 mM $K_2O_8S_2$ were prepared. Working solution was obtained by mixing equal volumes of the two stock solutions and allowed to stand in the dark at room temperature for 12 h. The ABTS radical working solution (1 mL) was diluted with 60 mL absolute methanol to obtain 1.1 ± 0.02 absorbance unit at a wavelength of 734 nm using the Helios Omega UV-vis spectrophotometer. Fresh ABTS radical working solution was prepared for each assay and the extraction solvent was used as control. Extract and control (150 µL each) was put into a clean centrifuge tube and 2.85 mL of ABTS radical working solution added. The mixture was shaken vigorously and allowed to stand for 10 min in the dark at room temperature. Absorbance of the incubated mixture was measured at 734 nm using absolute methanol as blank. Radical scavenging activity of ABTS was calculated using equation 4.

$$\text{ABTS RSA (\%)} = \left(\frac{A_C - A_E}{A_C}\right)100 \tag{4}$$

where A_E = absorbance of the reaction mixture containing extract, A_C = absorbance of control.

Determination of pasting properties

Pasting properties of the flour were determined in duplicate as described by Sun *et al.* (2014) using a Rapid Visco Analyser (RVA), model 4500 (Parten Instruments, Eden, Australia). Maize flour (3 g, corrected to 14% moisture basis) was weighed directly into a RVA canister and distilled water was added until a 28 g sample weight was attained. A standard programmed heating and cooling cycle was used. The programme was held for 1 min at 50 °C, heated to 95 °C at the rate of 12 °C/min, held at 95 °C for 2.7 min, cooled to 50 °C at the rate of 12 °C/min and held for 2 min at 50 °C. The pasting temperature (temperature at which viscosity increases over a 20 s period by at least 25 cP), peak viscosity (maximum hot paste viscosity), final viscosity (viscosity after cooling to 50 °C and

98

holding), trough viscosity (minimum viscosity at 95 °C), setback viscosity (final viscosity - trough viscosity) and breakdown viscosity (peak viscosity - trough viscosity) were recorded.

Statistical analysis

The data generated were subjected to analysis of variance (ANOVA) and the result presented as mean (±S.E) using a Statistica version 12 (StatSoft Inc, Oklahoma, USA). Level of significance was calculated using Fischer's least significant difference (LSD) test at 95% confidence interval. Principal component analysis (PCA), using XLSTAT software version 2015.1 (Addinsoft, Paris, France), was employed to explain the trend in variation and correlation among the samples and measured variables.

Results and discussion

Proximate composition

The moisture content of whole grain flours of the raw and roasted maize varieties, and that of the refined commercial maize meal (CMM) are presented in Table 5.2. The flour moisture content of the raw maize varieties ranged from 8.10% in urS28 to 11.02% in urH7D1, while that of CMM was 12.46%. For the roasted maize varieties, the range was between 12.50% in rH2G1 and 13.26% in rS33. There was no significant (p >0.05) difference between the moisture content of the raw and roasted maize varieties. This should be attributed to tempering of the maize grains before roasting. The moisture content of CMM did not significantly differ from that of rH2G1. However, the moisture content of CMM was significantly (p ≤0.05) higher than that of the raw maize varieties and lower than those of rS28, rS33 and rH7D1. Even though there was a significant difference in moisture content among the flours, the values were still within the recommended range of ≤13.50. It was reported that, for fungal growth to be inhibited, the moisture content of cereal grains should be <14% (Hoseney, 1994). The report by Humpf and Voss (2004) indicated that, the moisture content of ≤13.5% is recommended for proper storage of maize and its products.

The crude protein content of CMM (8.29%) was significantly lower than that of urS28 (8.57%), rS28 (8.68%), urS33 (8.66%), rS33 (8.90%), urH2G1 (9.11%), rH2G1 (9.27%), urH7D1 (9.02%) and rH7D1 (9.28%) maize varieties (Table 5.2). The Nigerian maize cultivars (S28 and S33) had significantly (p ≤0.05) lower crude protein content compared to that of the South African maize hybrids (H2G1 and H7D1). In each of the maize varieties, crude protein content of the roasted samples was higher than that of the unroasted, but the increase was not significant. Contrary to this, Oboh *et al.* (2010) reported significant decrease in protein content of maize roasted with electric hot plate. This contrasting findings could be due to differences in the roasting methods used. Lower crude protein content of CMM could be attributed to the removal of germ during milling for the production of meal, while higher protein in South African than in Nigerian maize could be related to varietal differences. The germ of maize kernel contains about 12% crude protein. Plant proteins constitute more than 70% of global protein consumption, and 71% of this comes from cereal grains

(Cerletti & Restani, 1985). Even though 75% of the crude protein in maize is found in the endosperm, the protein in germ contains most of the essential amino acids available. The germ of Brazilian maize contained more than 50% of the essential amino acid lysine (Naves *et al.*, 2011).

Crude oil content of the unroasted whole grain flour of the maize varieties ranged between 4.61% (urS28) and 5.05% (urH2G1) while that of the roasted maize ranged from 4.87% (rS33) to 5.06% (rH7D1) (Table 5.2). There was no significant difference between the crude oil content of the unroasted and roasted flour of each maize variety. FCR, thus, did not have a negative effect on the oil content of whole grain flour of the maize varieties. However, the oil content of CMM (0.91%) was significantly lower than that of the whole grain flours. The low content of oil in CMM is due to the removal of the germ during the milling process. The germ constitutes 12% of the maize kernel and contains approximately 25% oil. About 85% of the oil in the maize kernels is contained in the germ (CPT, 2015). Germ oil is considered the most valuable part of maize kernel because of its bland test and high content of the unsaturated fatty acid, linoleic acid (ω-6 fatty acid). Linoleic acid was reported to be the only essential ω-6 polyunsaturated fatty acid and is a precursor of eicosanoids (NAS, 2005). The dietary deficiency of linoleic acid is associated to scaly/rough skin and dermatitis

Ash content represents the inorganic components of food substances (AACC, 1999) which constitutes mineral elements. Bran and germ of cereal kernels are good sources of health promoting substances such as micronutrients (de Munter *et al.*, 2007). The mineral elements calcium, zinc and iron where found to be available in maize upon extraction of the ash with concentrated HCl and quantification by atomic absorption spectrophotometry (Naves *et al.*, 2011). In the refining process of grains, these micronutrients and other important components are removed. The ash content of CMM (0.35%) was, as expected, significantly lower than that of roasted and unroasted S28, S33, H2G1 and H7D1 whole grain flour (Table 5.2). There was no significant difference in ash content of the unroasted and roasted whole grain flour of each maize variety. Therefore, intermediate and finished food products produced from roasted whole grain maize flour would also be rich mineral elements (calcium, zinc and iron).

Carbohydrate, in the form of glucose, is the main energy source of humans for normal body functioning. Total carbohydrate content of whole grain flours of the unroasted and roasted maize varieties were significantly lower than that of CMM except urS28 which did not differ significantly (Table 5.2). However, the carbohydrate content of the roasted whole grain flour of each of the maize varieties significantly decreased. The decrease in carbohydrate content of the roasted maize could be due to the observed slight (non-significant) increase in crude protein, fiber and ash content.

Table 2 shows the crude fiber content which ranged from 1.36% (urS28) to 2.11% (urH2G1) for the raw, and from 1.47% (rS28) to 2.19% (rH2G1) for the roasted whole grain flours. As expected, the crude fiber content of CMM (0.39%) was significantly lower than that of the whole grain flours of the unroasted and roasted maize varieties, due to the removal of bran, which is largely dietary fiber. The South African maize hybrids (H2G1 and H7D1) contained significantly higher crude fiber than the Nigerian cultivars (S28 and S33). There was a non-significant increase in crude fiber content of

the roasted maize varieties compared to the unroasted. Fiber is the predominant organic component of bran and it comprises of hemicellulose (75%), cellulose (25%) and lignin (0.1%) (Dintzis *et al.*, 1985). Dietary fiber from whole grains, such as maize, was associated with a modest reduction of colorectal cancer (Schatzkin *et al.*, 2007; Aune *et al.*, 2011)

Table 5.2. Proximate composition of raw (ur) and roasted (r) whole grain flour of the S28, S33, H2G1 and H7D1 maize varieties, and that of refined commercial maize meal (CMM)

Sample	N	Moisture (%)	Dry matter (%)	Crude protein (%DM)	Crude oil (%DM)	Ash (%DM)	Carbohydrate (%DM)	Crude fiber (%)
urS28	10	8.10 ± 0.03^f	91.90 ± 0.07^a	8.57 ± 0.11^d	4.61 ± 0.06^b	1.11 ± 0.02^c	76.61 ± 0.15^a	1.36 ± 0.02^d
rS28	10	13.19 ± 0.07^a	86.81 ± 0.07^f	8.68 ± 0.07^d	4.91 ± 0.08^{ab}	1.15 ± 0.01^{bc}	72.07 ± 0.15^d	1.47 ± 0.05^d
urS33	10	8.71 ± 0.04^e	91.29 ± 0.04^b	8.66 ± 0.05^{cd}	4.85 ± 0.14^{ab}	1.04 ± 0.01^d	76.74 ± 0.15^b	1.77 ± 0.10^c
rS33	10	13.26 ± 0.08^a	86.74 ± 0.08^f	8.90 ± 0.06^{bc}	4.87 ± 0.12^{ab}	1.05 ± 0.02^d	71.92 ± 0.14^d	1.79 ± 0.05^c
urH2G1	10	10.69 ± 0.07^d	89.31 ± 0.07^c	9.11 ± 0.08^{ab}	5.08 ± 0.10^a	1.20 ± 0.02^a	73.92 ± 0.16^c	2.11 ± 0.03^{ab}
rH2G1	10	12.50 ± 0.15^c	87.50 ± 0.15^d	9.27 ± 0.03^a	4.96 ± 0.05^a	1.22 ± 0.01^a	72.04 ± 0.20^d	2.19 ± 0.05^a
urH7D1	10	11.02 ± 0.07^d	88.99 ± 0.07^c	9.02 ± 0.04^{ab}	4.92 ± 0.04^{ab}	1.19 ± 0.01^{ab}	73.87 ± 0.11^c	1.98 ± 0.02^b
rH7D1	10	12.84 ± 0.14^b	87.16 ± 0.14^e	9.28 ± 0.05^a	5.06 ± 0.12^a	1.20 ±0.01^a	71.63 ± 0.21^d	2.07 ± 0.07^{ab}
CMM	10	12.46 ± 0.10^c	87.54 ± 0.10^d	8.29 ± 0.15^e	0.91 ± 0.07^c	0.35 ± 0.02^e	77.98 ± 0.20^a	0.39 ± 0.01^e

Values are presented as means (± S.E) and N = number of samples. Values with different superscripts along a column are significantly (p ≤0.05) different.

Antioxidant content and activity

Total phenolics content of the unroasted and roasted whole grain flour of the maize varieties and that of CMM are presented in Table 5.3. The phenolics content of the unroasted maize ranged from 16.13 mg GAE/g in urS33 to 19.77 mg GAE/g in urH7D1, while that of the roasted maize ranged between 16.14 mg GAE/g in rS33 and 18.66 mg GAE/g in rH7D1. There was a non-significant decrease in total phenolics of S28 and an increase in that of S33 and H7D1 after roasting, while that of H2G1 significantly increased. However, the total phenolics content of CMM (3.84 mg GAE/g) was significantly lower than that of the whole grain maize varieties. It was also observed that H2G1 and H7D1 (hard maize kernels) contained significantly higher amount of phenolics than S28 and S33 (soft maize kernels). Chiremba *et al.* (2012) investigated the phenolics content of soft and hard maize varieties and reported that the bran of hard maize types contained significantly higher phenolics than the soft maize varieties. Increase in total phenolics of rH2G1 could be attributed to the production of new compounds with phenolics-like structures (melanoidins) by Maillard reaction as reported by Lemos *et al.* (2012). The unroasted and roasted whole grain flours of each of the maize varieties did not significantly differ in total flavonoids content (Table 5.3). However, the total flavonoids content of CMM was found to be significantly lower. Forced convection roasting did not have a negative effect on total flavonoids content of the maize varieties. Lower content of total phenolics and flavonoids in CMM is associated with the removal of bran during the refining process. Phenolics and flavonoids are concentrated in the bran of cereal grains (Adom & Liu, 2002).

Antioxidant activity of plant material is best assessed using free radical scavenging of DPPH and ABTS stable radicals by the available phenolic compounds (Das & Singh, 2015). The DPPH and ABTS radical scavenging activity of CMM, unroasted and roasted S28, S33, H2G1 and H7D1 maize varieties were investigated and the result presented in Table 5.3. Ability of the phenolic compounds to scavenge the DPPH and ABTS radicals was expressed in percentage (%), where higher % indicates greater ability. The DPPH and ABTS radical scavenging activities of CMM were significantly lower than those of the whole grain flours of the maize varieties. Furthermore, the DPPH antioxidant activity of unroasted and roasted whole grain flours of each of the maize varieties did not differ significantly. Similar trend was observed for ABTS antioxidant activity, which showed non-negative effect of FCR. The result indicated that, the antioxidants (phenolics and flavonoids) in the whole grain flours of the maize varieties had greater capacity to scavenge or neutralise the detrimental effects of ABTS radicals more efficiently than DPPH radicals. The capacity of antioxidants in unroasted and roasted whole grain flour of S28, S33, H2G1 and H7D1 to scavenge ABTS radicals was found to be >98%, which was significantly higher than that of CMM (27.12%). Similarly, the DPPH scavenging capacity of the antioxidants ranged from 60.32% in urS33 to 66.15% in rH7D1 which were also significantly higher than that of CMM (20.53%). Removal of bran during the refining process was the reason for low free radical scavenging capacity of CMM. Higher quantity of phenolic compounds was related to greater free radical scavenging activity (Kim *et al.*, 2011), as also observed in this study. Phenolic compounds are able to act as antioxidants because of their

ability to donate a proton from the hydroxyl group to free radicals, resulting in the formation of stable phenoxyl radicals that are harmless (Das & Singh, 2015). Due to the high content of phenolic compounds in the bran of cereal grains, whole grain consumption was found to be related to reduced risk of hypertension (Wang *et al.*, 2007), blood pressure (Behall *et al.*, 2006), and ischemic and coronary heart diseases (Jacobs *et al.*, 1998; Jensen *et al.*, 2004).

Table 5.3. Total phenolics and flavonoids content, and DPPH and ABTS radical scavenging activities of raw (ur) and roasted (r) whole grain flour of S28, S33, H2G1 and H7D1 maize varieties, and commercial maize meal (CMM)

Sample	N	Total phenolics (mg GAE/g DM)	Total flavonoids (mg CE/g DM)	DPPH (%)	ABTS (%)
urS28	10	16.98 ± 0.42[c]	0.51 ± 0.02[a]	65.51 ± 0.40[a]	99.41 ± 0.07[ab]
rS28	10	16.68 ± 0.54[c]	0.48 ± 0.01[ab]	65.43 ± 0.78[a]	99.42 ± 0.02[ab]
urS33	10	16.13 ± 0.54[d]	0.30 ± 0.02[e]	60.32 ± 0.68[bc]	99.47 ± 0.08[b]
rS33	10	16.14 ± 0.26[d]	0.33 ± 0.01[e]	62.13 ± 1.15[c]	98.95 ± 0.06[ab]
urH2G1	10	18.66 ± 0.31[a]	0.43 ± 0.01[cd]	64.94 ± 0.67[ab]	99.63 ± 0.03[a]
rH2G1	10	19.77 ± 0.10[b]	0.43 ± 0.01[d]	64.16 ± 0.41[a]	99.58 ± 0.02[ab]
urH7D1	10	19.12 ± 0.25[ab]	0.48 ± 0.02[ab]	65.15 ± 0.43[a]	99.43 ± 0.05[ab]
rH7D1	10	19.24 ± 0.24[ab]	0.47 ± 0.01[bc]	66.15 ± 0.28[a]	99.48 ± 0.03[ab]
CMM	10	3.84 ± 0.31[e]	0.12 ± 0.01[f]	20.53 ± 0.57[d]	27.12 ± 0.57[c]

Values are presented as means (± S.E) and N = number of samples. Values with different superscripts along a column are significantly ($p ≤ 0.05$) different.

Pasting properties

The pasting temperature, peak viscosity, final viscosity, trough viscosity, setback viscosity and breakdown viscosity of CMM and whole grain flours of the unroasted and roasted maize varieties were assessed and the result presented in Table 5.4. There was a decrease in pasting temperature of each maize variety due to roasting, but the decrease was not significant. The pasting temperature of the whole grain flours of the maize varieties (unroasted and roasted) was significantly higher than that of CMM. Significantly higher pasting viscosities (peak, final, trough, setback and breakdown) were observed in CMM compared to the whole grain flours of the unroasted and roasted maize varieties. Refined flour contains higher quantity of starch than that of a whole grain flour (Ragaee & Abdel-Aal, 2006) which would be responsible for higher pasting viscosities such as observed for the CMM. After FCR, significant increase in pasting viscosities of whole grain flour of each of the maize varieties was observed. Higher pasting temperatures and lower viscosities observed in the whole grain flour of the maize varieties than CMM could be attributed to lower rate of water absorption and swelling capacity of starch granules as corroborated by Ragaee and Abdel-Aal (2006).

The whole grain maize flour contained high quantity of fiber (resistant starch) which affects pasting properties. Inclusion of 5% fiber into wheat starch significantly decreased peak, breakdown and final viscosities (Symons & Brennan, 2004). The first holding period in RVA process subjects starch slurry to high temperature and shear stress resulting in disruption of granules, leaching and alignment of amylose molecules. This leads to peak viscosity which is directly proportional to breakdown. Re-association between starch (amylose and short chain amylopectin) molecules causes the formation of gel structure, characteristic of 'Pap' and 'Tuwo' (processed maize products), which occurs at final viscosity. Then reordering and retrogradation of starch molecules take place in a process called setback, which was lower in the whole grain flour. The low viscosities observed in the whole grain flour of the maize varieties was an indication of poor gelling characteristic and less paste stability compared to that of CMM. However, the decrease in pasting temperature (though, not significant) and significant increase in pasting viscosities of the whole grain flours of roasted maize compared to the unroasted is an indication of better gelling quality of the roasted whole grain flour.

Table 5.4. Pasting properties of raw (ur) and roasted (r) whole grain flour of S28, S33, H2G1 and H7D1 maize varieties, and commercial maize meal (CMM)

Sample	N	Pasting temperature (ºC)	Pasting viscosity (cP)	Final viscosity (cP)	Trough viscosity (cP)	Setback viscosity (cP)	Breakdown viscosity (cP)
urS28	10	84.01 ± 0.67[a]	624.30 ± 08.42[d]	1007.50 ± 03.83[e]	457.20 ± 06.01[f]	550.30 ± 06.79[d]	167.10 ± 06.97[bc]
rS28		83.87 ± 0.44[a]	790.25 ± 31.46[c]	1881.65 ± 35.20[d]	650.85 ± 28.97[d]	530.80 ± 11.87[cd]	139.40 ± 07.52[c]
urS33	10	80.60 ± 0.45[c]	673.00 ± 14.14[d]	1022.40 ± 13.65[e]	484.20 ± 14.67[f]	538.20 ± 13.27[bd]	188.80 ± 25.38[bc]
rS33		80.40 ± 0.49[c]	926.25 ± 12.79[b]	1373.85 ± 25.99[bc]	788.20 ± 12.22[c]	585.65 ± 15.67[b]	138.05 ± 04.15[c]
urH2G1	10	82.67 ± 0.66[b]	814.70 ± 04.95[c]	1086.50 ± 19.76[de]	575.80 ± 16.21[e]	510.70 ± 6.92[de]	238.90 ± 15.50[b]
rH2G1		82.47 ± 0.63[b]	946.25 ± 18.38[b]	1334.40 ± 38.66[c]	808.40 ± 19.75[bc]	526.00 ± 20.60[d]	137.85 ± 05.35[c]
urH7D1	10	81.18 ± 0.41[c]	836.70 ± 13.52[c]	1107.60 ± 31.06[de]	637.10 ± 15.78[de]	470.50 ± 6.92[e]	199.60 ± 23.60[bc]
rH7D1		80.85 ± 0.58[bc]	988.10 ± 19.88[b]	1420.85 ± 38.29[b]	848.85 ± 20.96[b]	572.00 ± 22.52[bc]	139.25 ± 05.00[c]
CMM	10	75.34 ± 0.19[d]	1604.90 ± 47.54[a]	2518.45 ± 22.98[a]	1095.00 ± 11.00[a]	1423.45 ± 12.60[a]	509.90 ± 43.78[a]

Values are presented as means (± S.E) and N = number of samples. Values with different superscripts along a column are significantly ($p \leq 0.05$) different.

Principal component analysis (PCA)

PCA of the data, after auto scaling, was carried out and Fig. 5.1 shows the explained variation of eight principal components (PC). The cumulative variation explained by PC1 (F1) and PC2 (F2) were 69.85% and 22.73%, respectively, with a total of 92.59% (Fig. 5.2). PC1 and PC2 were used for the construction of PCA plots (scores, loadings and biplot) which illustrated an overview of the variations and interrelationships among samples and the measured variables. Distance between any two of the samples on the plot is directly proportional to their extent of similarities or differences. Considering PC1, CMM was distinctly separated (negative correlation) from the whole grain flours of the unroasted and roasted maize grains (Fig. 5.2). Among the whole grain flours, it could be observed that the roasted samples (rS33, rS28, rH2G1 and rH7D1) are grouped separately from the unroasted (urH7D1, urH2G1 and urS28, urS33) (Fig. 5.2). This indicated strong positive correlation of samples in each group. CMM was more associated with high peak and final viscosities, carbohydrate and moisture content, lower content of dry matter (DM), DPPH, ABTS, total flavonoids (TF), oil, ash, total phenolics (TP), fiber, pasting temperature (PT) and protein compared to the whole grain flour (Fig. 5.3). Furthermore, rS28, rS33, rH2G1 and rH7D1 were more associated with high protein content, fiber, PT, oil and ash while urH7D and urH2G1 were more related to high TF, DPPH and ABTS, and urS28 and urS33 to high DM and carbohydrate content (Fig. 5.3).
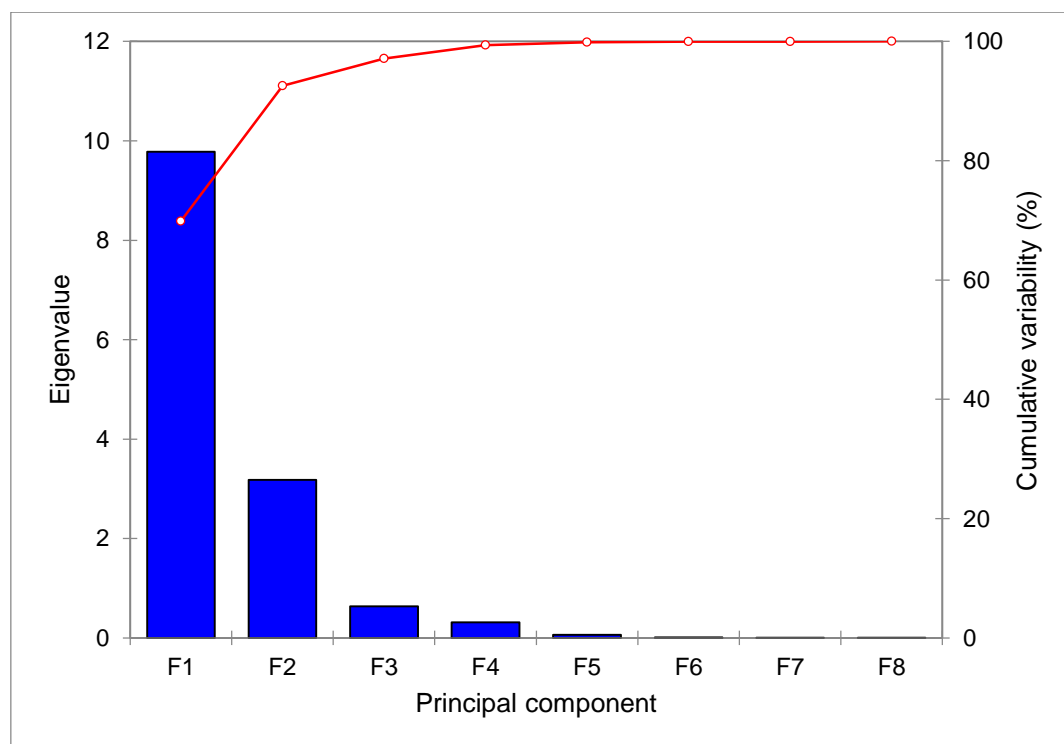

Figure 5.1. Scree plot showing the eight principal components (F1 – F8) and their percent cumulative variabilities that explained the variations and interrelationships among samples and the measured variables
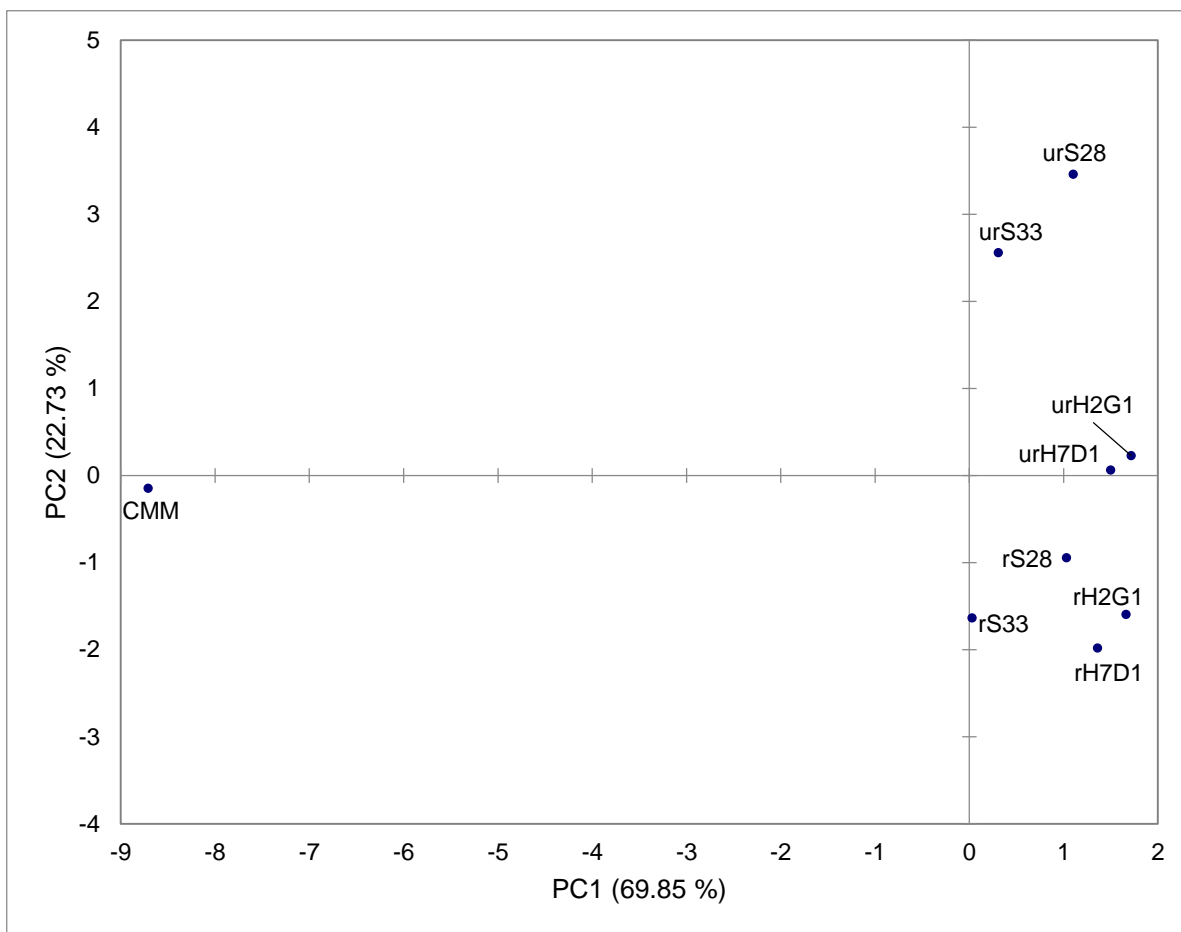
Figure 5.2. Scores plot showing separation (grouping) of the samples (CMM, unroasted and roasted maize) according to their variations and relationships.
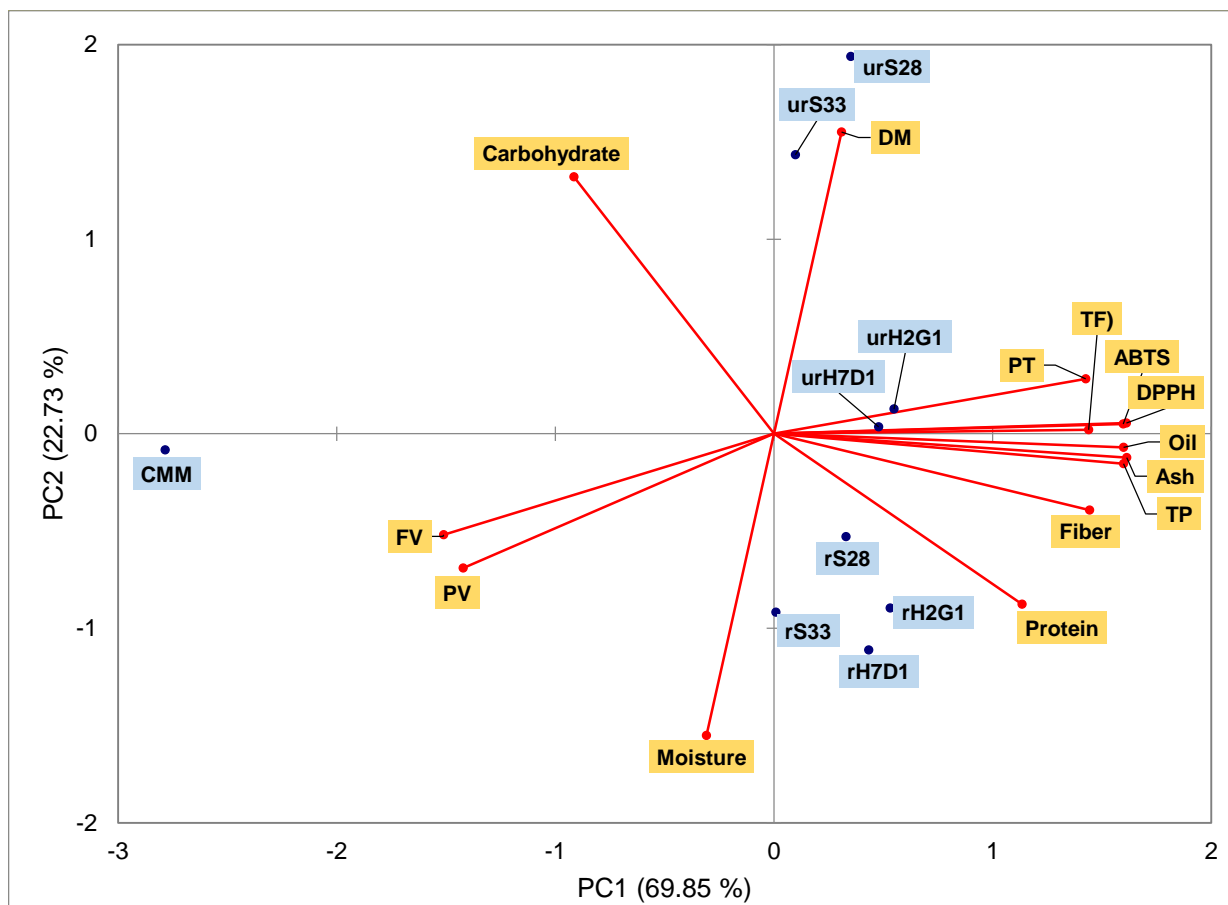
Figure 5.3. Biplot (combination of scores and loadings plots) showing the variations and relationships among the samples and measured variables.

Correlation analysis of measured variables

Pearson's (n) correlation analysis was conducted at 95% confidence interval to study how the measured variables correlate with each other and the results are presented in Table 5.5. Crude fiber content was highly positively correlated to ash, total phenolics, total flavonoids, DPPH, ABTS and pasting temperature. Crude protein content showed moderate negative correlation with carbohydrate and high positive correlation with crude oil content. There was a high positive correlation of total phenolics with total flavonoids content, DPPH and ABTS antioxidant activity. Furthermore, crude fiber had moderate negative correlation with carbohydrate and high positive correlation with peak and final viscosities. The correlation of pasting temperature with peak and final viscosities was found to be moderately negative.

Table 5.5 Correlation matrix (Pearson [n]) at 95% confidence interval of the measured variables of whole grain flour of raw (ur) and roasted (r) S28, S33, H2G1 and H7D1 maize varieties, and commercial maize meal (CMM)

Number	Variable	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Moisture (%)	1													
2	Dry matter (%)	-1.000	1												
3	Crude protein (%DM)	0.455	-0.455	1											
4	Ash (%)	-0.122	0.122	0.603	1										
5	Crude oil (%DM)	-0.149	0.149	0.558	0.980	1									
6	Carbohydrate (%DM)	-0.710	0.710	-0.828	-0.601	-0.582	1								
7	Crude fiber (%)	-0.012	0.012	0.829	0.908	0.897	-0.664	1							
8	TP (mg GAE/g DM)	-0.085	0.085	0.662	0.992	0.971	-0.631	0.933	1						
9	TF (mg CE/g DM)	-0.154	0.154	0.374	0.897	0.825	-0.454	0.675	0.870	1					
10	DPPH (%)	-0.208	0.208	0.488	0.986	0.989	-0.524	0.857	0.970	0.887	1				
11	ABTS (%)	-0.204	0.204	0.490	0.972	0.996	-0.529	0.865	0.956	0.830	0.993	1			
12	PT (˚C)	0.109	-0.109	0.530	0.857	0.839	-0.672	0.726	0.856	0.762	0.837	0.820	1		
13	PV (cP)	0.537	-0.537	-0.120	-0.832	-0.876	0.155	-0.637	-0.799	-0.752	-0.903	-0.908	-0.701	1	
14	FV (cP)	0.464	-0.464	-0.271	-0.898	-0.927	0.264	-0.745	-0.882	-0.797	-0.945	-0.946	-0.761	0.984	1

TP = total phenolics, TF = total flavonoids, PT = pasting temperature, PV = pasting viscosity, FV = final viscosity, ABTS = [2,2′-Azino-bis(3-ethylbenzoline-6-sulfonic acid) diammonium radical scavenging activity, DPPH = 2,2-diphenyl-1-picrylhydrazyl radical scavenging activity.

Conclusion

Proximate composition indicated that there was no significant difference in crude protein, crude oil, ash and crude fiber of the whole grain flours between the unroasted and roasted maize varieties. Similarly, the protein, oil, ash and fiber of the unroasted and roasted whole grain flours of the maize varieties were found to be significantly higher than those of the CMM. However, due to the removal of bran and germ during refining process of CMM, its carbohydrate content was found to be significantly higher than that of the unroasted and roasted S28, S33, H2G1 and H7D1 whole grain flours. As a result of this, the total phenolics and flavonoids content as well as DPPH and ABTS free radical scavenging capacity of the whole grain flours were significantly higher than those of CMM. Furthermore, the total phenolics content of whole grain flours of the roasted maize varieties did not differ significantly, except that of H2G1 which showed significant increase. However, there was no significant difference in total flavonoids, DPPH and ABTS antioxidant capacity between the unroasted and roasted whole grain flours. All the pasting viscosities (peak, final, breakdown, trough and setback) of whole grain flours of the roasted were significantly higher than those obtained in the unroasted maize varieties. Pasting temperatures did not show significant difference between whole grain flours of the unroasted and roasted maize varieties. Whole grain flours of the unroasted and roasted maize varieties had significantly lower pasting temperatures and higher pasting viscosities than the CMM. Non-significant difference in protein, oil, ash and fiber content, antioxidant activity, pasting temperatures, and significantly higher pasting viscosities of whole grain flours of the roasted than the unroasted maize varieties indicated the effectiveness of FCR for value addition to the end product. High proximate composition (protein, oil, fiber, ash) and phytochemicals (phenolics and flavonoids) as well as antioxidant activity of the whole grain flours demonstrated superior nutritional quality compared to CMM.

References

AACC (1999). *Approved methods of the american association of cereal chemists international.* St. Paul, Minnesota, USA: AACC International.

Adom, K.K. & Liu, R.H. (2002). Antioxidant activity of grains. *Journal of Agricultural and Food Chemistry,* **50,** 6182-6187.

AOAC (2002). *Official methods of analysis of the association of official analytical chemists international.* Arlington, Virginia, USA: AOAC International.

Aune, D., Chan, D., Lau, R., Vieira, R., Greenwood, D.C., Kampman, E. & Norat, T. (2011). Dietary fibre, whole grains, and risk of colorectal cancer: Systematic review and dose-response meta-analysis of prospective studies. *British Medical Journal,* **343,** 1-20.

Ayatse, J.O., Eka, O.U. & Ifon, E.T. (1983). Chemical evaluation of the effect of roasting on the nutritive value of maize (*Zea mays* Linn.). *Food Chemistry,* **12,** 135-147.

Behall, K.M., Scholfield, D.J. & Hallfrisch, J. (2006). Whole-grain diets reduce blood pressure in mildly hypercholesterolemic men and women. *Journal of the American Dietetic Association,* **106,** 1445-1449.

Cerletti, P. & Restani, P. (1985). Maize germ proteins, their composition, nutritive value and functional properties. In: *Amino acid composition and biological value of cereal proteins* (edited by Lásztity, R. & Hidvégi, M.). Springer Netherlands.

Chiremba, C., Taylor, J.R.N., Rooney, L.W. & Beta, T. (2012). Phenolic acid content of sorghum and maize cultivars varying in hardness. *Food Chemistry,* **134,** 81-88.

Chung, H.-S., Chung, S.-K. & Youn, K.-S. (2011). Effects of roasting temperature and time on bulk density, soluble solids, browning index and phenolic compounds of corn kernels. *Journal of Food Processing and Preservation,* **35,** 832-839.

CPT (2015). Corn kernel composition. Cereal Process Technologies. URL: http://www.cerealprocess.com/fractionation/ Accessed 01/June/2015.

Das, A.K. & Singh, V. (2015). Antioxidative free and bound phenolic constituents in pericarp, germ and endosperm of indian dent (*Zea mays* Var. Indentata) and flint (*Zea mays* Var. Indurata) maize. *Journal of Functional Foods,* **13,** 363-374.

De Munter, J.S., Hu, F.B., Spiegelman, D., Franz, M. & Van Dam, R.M. (2007). Whole grain, bran, and germ intake and risk of type 2 diabetes: A prospective cohort study and systematic review. *PLoS Medicine,* **4,** 1385-1395.

Dintzis, F.R., Watson, P.R. & Sandstead, H.H. (1985). Mineral contents of brans passed through the human gi tract. *The American Journal of Clinical Nutrition,* **41,** 901-908.

Harris, K.A. & Kris-Etherton, P.M. (2010). Effects of whole grains on coronary heart disease risk. *Current Atherosclerosis Reports,* **12,** 368-376.

Hoover, R. & Manuel, H. (1996). The effect of heat–moisture treatment on the structure and physicochemical properties of normal maize, waxy maize, dull waxy maize and amylomaize v starches. *Journal of Cereal Science,* **23,** 153-162.

Hoseney, R.C. (1994). *Principles of cereal science and technology.* St. Paul, Minnesota, USA: American Association of Cereal Chemists (AACC).

Humpf, H.-U. & Voss, K.A. (2004). Effects of thermal food processing on the chemical structure and toxicity of fumonisin mycotoxins. *Molecular Nutrition and Food Research,* **48,** 255-269.

Jacobs, D., Meyer, K.A., Kushi, L.H. & Folsom, A.R. (1998). Whole-grain intake may reduce the risk of ischemic heart disease death in postmenopausal women: The iowa women's health study. *The American Journal of Clinical Nutrition,* **68,** 248-257.

Jenkins, P.J. & Donald, A.M. (1998). Gelatinisation of starch: A combined SAXS/WAXS/DSC and sans study. *Carbohydrate Research,* **308,** 133-147.

Jensen, M.K., Koh-Banerjee, P., Hu, F.B., Franz, M., Sampson, L., Grønbæk, M. & Rimm, E.B. (2004). Intakes of whole grains, bran, and germ and the risk of coronary heart disease in men. *The American Journal of Clinical Nutrition,* **80,** 1492-1499.

Karioti, A., Hadjipavlou-Litina, D., Mensah, M.L., Fleischer, T.C. & Skaltsa, H. (2004). Composition and antioxidant activity of the essential oils of *Xylopia aethiopica* (Dun) A. Rich. (Annonaceae) leaves, stem bark, root bark, and fresh and dried fruits, growing in ghana. *Journal of Agricultural and Food Chemistry,* **52,** 8094-8098.

Katcher, H.I., Legro, R.S., Kunselman, A.R., Gillies, P.J., Demers, L.M., Bagshaw, D.M. & Kris-Etherton, P.M. (2008). The effects of a whole grain–enriched hypocaloric diet on cardiovascular disease risk factors in men and women with metabolic syndrome. *The American Journal of Clinical Nutrition,* **87,** 79-90.

Kim, H.G., Kim, G.W., Oh, H., Yoo, S.Y., Kim, Y.O. & Oh, M.S. (2011). Influence of roasting on the antioxidant activity of small black soybean (*Glycine max* L. Merrill). *LWT - Food Science and Technology,* **44,** 992-998.

Lee, S. & Lee, J. (2009). Effects of oven-drying, roasting, and explosive puffing process on isoflavone distributions in soybeans. *Food Chemistry,* **112,** 316-320.

Lemos, M.R.B., Siqueira, E.M.D.A., Arruda, S.F. & Zambiazi, R.C. (2012). The effect of roasting on the phenolic compounds and antioxidant potential of baru nuts [*Dipteryx alata* Vog.]. *Food Research International,* **48,** 592-597.

Maki, K.C., Beiseigel, J.M., Jonnalagadda, S.S., Gugger, C.K., Reeves, M.S., Farmer, M.V., Kaden, V.N. & Rains, T.M. (2010). Whole-grain ready-to-eat oat cereal, as part of a dietary program for weight loss, reduces low-density lipoprotein cholesterol in adults with overweight and obesity more than a dietary program including low-fiber control foods. *Journal of the American Dietetic Association,* **110,** 205-214.

Melanson, K.J., Angelopoulos, T.J., Nguyen, V.T., Martini, M., Zukley, L., Lowndes, J., Dube, T.J., Fiutem, J.J., Yount, B.W. & Rippe, J.M. (2006). Consumption of whole-grain cereals during weight loss: Effects on dietary quality, dietary fiber, magnesium, vitamin B-6, and obesity. *Journal of the American Dietetic Association,* **106,** 1380-1388.

Mellen, P.B., Walsh, T.F. & Herrington, D.M. (2008). Whole grain intake and cardiovascular disease: A meta-analysis. *Nutrition, Metabolism and Cardiovascular Diseases,* **18,** 283-290.

NAS (2005). *Dietary reference intakes for energy, carbohydrate, fiber, fat, fatty acids, cholesterol, protein, and amino acids (macronutrients).* National Academy of Science, Washington, D.C: National Academies Press.

Naves, M.M.V., Castro, M.V.L.D., Mendonça, A.L.D., Santos, G.G. & Silva, M.S. (2011). Corn germ with pericarp in relation to whole corn: Nutrient contents, food and protein efficiency, and protein digestibility-corrected amino acid score. *Food Science and Technology (Campinas),* **31,** 264-269.

NCM (2015). National chamber of milling, South Africa. URL: http://www.grainmilling.org.za/ Accessed 6/May/2015.

Nettleton, J.A., Steffen, L.M., Loehr, L.R., Rosamond, W.D. & Folsom, A.R. (2008). Incident heart failure is associated with lower whole-grain intake and greater high-fat dairy and egg intake

in the atherosclerosis risk in communities (ARIC) study. *Journal of the American Dietetic Association,* **108,** 1881-1887.

Oboh, G., Ademiluyi, A.O. & Akindahunsi, A.A. (2010). The effect of roasting on the nutritional and antioxidant properties of yellow and white maize varieties. *International Journal of Food Science and Technology,* **45,** 1236-1242.

Ragaee, S. & Abdel-Aal, E.-S.M. (2006). Pasting properties of starch and protein in selected cereals and quality of their food products. *Food Chemistry,* **95,** 9-18.

Ranum, P., Peña-Rosas, J.P. & Garcia-Casal, M.N. (2014). Global maize production, utilization, and consumption. *Annals of the New York Academy of Sciences,* **1312,** 105-112.

Schatzkin, A., Mouw, T., Park, Y., Subar, A.F., Kipnis, V., Hollenbeck, A., Leitzmann, M.F. & Thompson, F.E. (2007). Dietary fiber and whole-grain consumption in relation to colorectal cancer in the nih-aarp diet and health study. *The American Journal of Clinical Nutrition,* **85,** 1353-1360.

Stevenson, D.G., Biswas, A. & Inglett, G.E. (2005). Thermal and pasting properties of microwaved corn starch. *Starch-Stärke,* **57,** 347-353.

Sun, Q., Xing, Y., Qiu, C. & Xiong, L. (2014). The pasting and gel textural properties of corn starch in glucose, fructose and maltose syrup. *Public Library of Science One,* **9,** 1-6.

Symons, L. & Brennan, C. (2004). The effect of barley β-glucan fiber fractions on starch gelatinization and pasting characteristics. *Journal of Food Science,* **69,** 257-261.

Thaipong, K., Boonprakob, U., Crosby, K., Cisneros-Zevallos, L. & Hawkins Byrne, D. (2006). Comparison of abts, dpph, frap, and orac assays for estimating antioxidant activity from guava fruit extracts. *Journal of Food Composition and Analysis,* **19,** 669-675.

Wang, L., Chen, J., Xie, H., Ju, X. & Liu, R.H. (2013). Phytochemical profiles and antioxidant activity of adlay varieties. *Journal of Agricultural and Food Chemistry,* **61,** 5103-5113.

Wang, L., Gaziano, J.M., Liu, S., Manson, J.E., Buring, J.E. & Sesso, H.D. (2007). Whole-and refined-grain intakes and the risk of hypertension in women. *The American Journal of Clinical Nutrition,* **86,** 472-479.

Yang, J., Martinson, T.E. & Liu, R.H. (2009). Phytochemical profiles and antioxidant activities of wine grapes. *Food Chemistry,* **116,** 332-339.

Youn, K.-S. & Chung, H.-S. (2012). Optimization of the roasting temperature and time for preparation of coffee-like maize beverage using the response surface methodology. *LWT - Food Science and Technology,* **46,** 305-310.

Žilić, S., Serpen, A., Akıllıoğlu, G., Gökmen, V. & Vančetović, J. (2012). Phenolic compounds, carotenoids, anthocyanins, and antioxidant capacity of colored maize (*Zea mays* L.) kernels. *Journal of Agricultural and Food Chemistry,* **60,** 1224-1231.
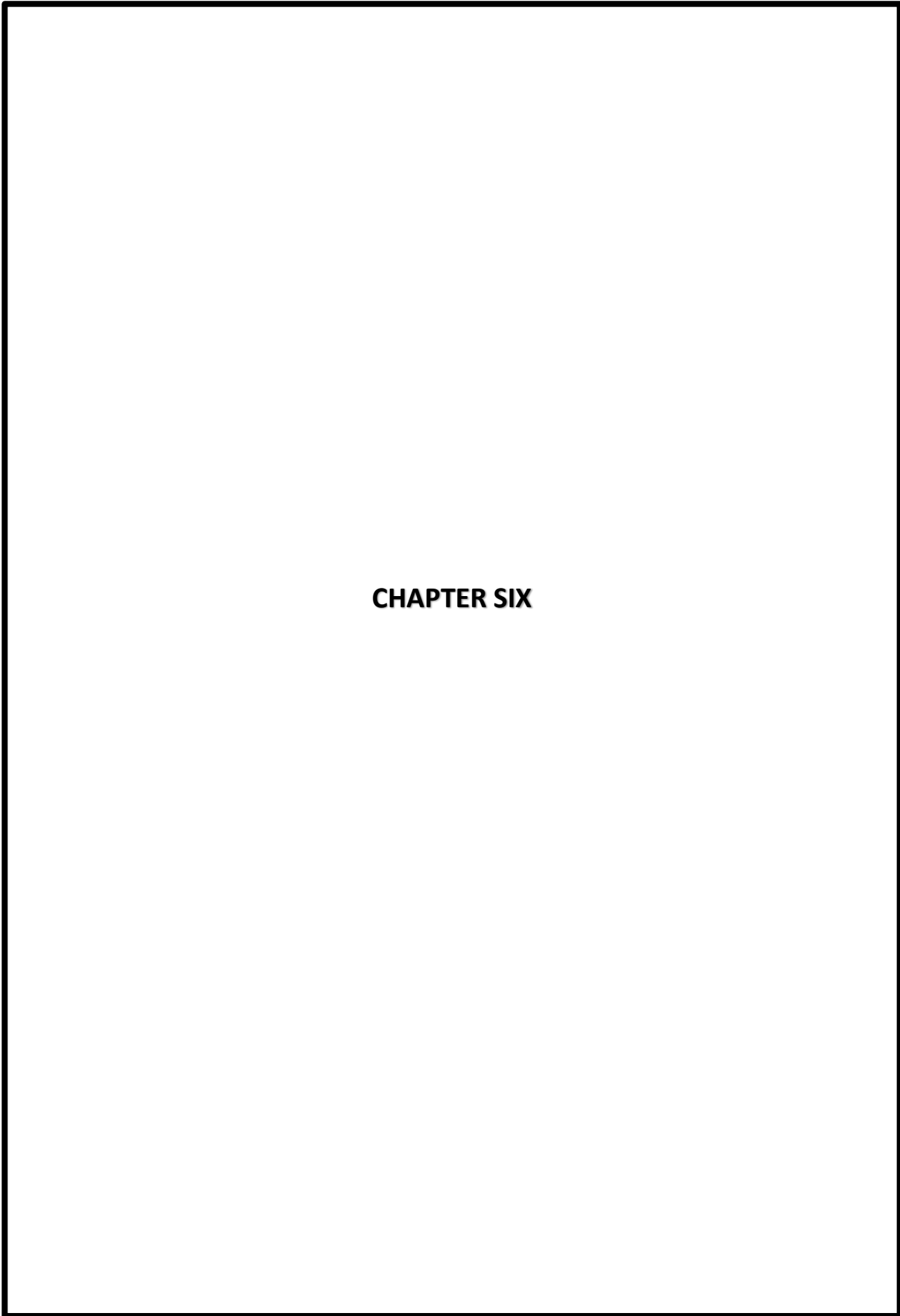
CHAPTER SIX

CHARPTER 6

General discussion and conclusions

The most widely cultivated cereal crop in the world is maize (*Zea mays* L.). In developed countries such as USA larger quantity of maize cultivated is utilised for the production of animal feed and as raw material for food, confectionery, pharmaceutical and related factories. However, in developing nations such as Nigeria and South Africa as well as many poor countries, maize is predominantly consumed as staple food by humans. Maize flour and meal are the most important intermediate (preprocessed) products used for the production of 'Tuwo' and 'Mielie pap' among others in Western Africa (Nigeria, Niger, Ghana) and Southern Africa (South Africa, Lesotho, Zimbabwe), respectively, which are consumed with different types of vegetable soup.

The maize flour and meal consumed are not pregelatinised and do not contain bran and germ, which are removed during refining process. Removal of bran (source of dietary fiber, phytochemicals and minerals) and germ (source of protein with high content of essential amino acids, vitamins, minerals and unsaturated fatty acids) deprives consumers of their nutritional benefits. O'Neil *et al.* (2010) reported consumption of whole grain cereal products to be associated with high nutrient intake and better diet quality. Similarly consumption of whole grains was shown to significantly reduce the risk of cardiovascular diseases, certain cancers, type 2 diabetes mellitus, obesity, stroke and hypertension (Jensen *et al.*, 2004; de Munter *et al.*, 2007; Schatzkin *et al.*, 2007; Good *et al.*, 2008). Conversion of whole grains into intermediate and finished food products for human consumption requires the use of heat. Maize grains can be heat-processed by roasting, boiling, extrusion and nixtamalisation (Bolade *et al.*, 2009).

Roasting is a processing method that uses dry heat (Oliviero *et al.*, 2008) which led to changes in properties such as physicochemical, nutritional and phytochemical. The use of dry heat in roasting was reported to be associated with the reduction in nutritional quality of end products by causing decrease in essential amino acids (Özdemir *et al.*, 2001), protein, dietary fiber and phenolic compounds (Oboh *et al.*, 2010). Effect of forced convection roasting (FCR), a novel roasting technique that has the additional advantage of using superheated steam and continued tumbling of grains which ensures effective and uniform roasting, on physicochemical, nutritional and antioxidant properties of Nigerian (S28, S33) and South African (H2G1, H7D1) maize varieties was studied. FCR conditions (roasting temperature and rotating speed [determining time of roasting]) were optimised and used for the production of whole grain flour or meal. To achieve these, central composite design, response surface methodology and desirability profiling were employed. The roasting temperature and rotating speed limits used were (150 to 220 °C) and (30 to 90 Hz), respectively, obtained from preliminary roasting experiments. Proximate composition, antioxidant and pasting properties of whole grain flours produced using the optimum roasting conditions were

116

assessed and compared to those of raw maize whole grain flours and a refined commercial unroasted maize meal (CCM).

Results of the study indicated that FCR had no effect on the protein content, TEAA and antioxidant (content and activity) properties of Nigerian maize cultivars, except TAA of S28, which significantly increased with increase in temperature. For the South African maize hybrids, protein content, total flavonoids and antioxidant activity were not affected except the total phenolics content of H2G1 which significantly increased with an increase in roasting temperature and rotating speed. The increase in total phenolics observed in H2G1 did not result in increase in antioxidant activity. Formation of new substances such as melanoidins (with phenolics like structures) by Maillard reaction during roasting may enhance antioxidant activity (Lemos *et al.*, 2012). This means that the substances responsible for the increase in total phenolics of H2G1 did not have antioxidant activity. The changes observed in physicochemical properties of the maize varieties such as bulk density, kernel hardness, pH and colour did not negatively affect the quality of the whole grain flours produced. Conventional roasting of grains using dry hot-air (dry heat) was found to be associated with loss of vitamins and essential amino acids as well as decrease in protein and carbohydrate digestibility (Jinap *et al.*, 1998; Özdemir & Devres, 1999; Özdemir *et al.*, 2001).

Prediction models of all the response variables studied were assessed and their coefficient of determination (R^2) and lack-of-fit determined. The models for whiteness index (WI), yellowness index (YI) , total essential amino acids (TEAA) and total amino acids (TAA) with good fit (R^2 >0.8) and non-significant (p >0.05) lack-of-fit were selected and subjected to desirability profiling at recommended moisture content of ≤13.50 (Humpf & Voss, 2004) for the optimisation of roasting conditions. It was reported that, prediction model will have a good fit with experimental data if the value of its R^2 is ≥0.8 and lack-of-fit is non-significant (Guan & Yao, 2008). Furthermore, the models of these response variables were selected because of their benefits. Amino acids serve as building blocks (monomers) in the construction of polypeptide chains of proteins (Westermann *et al.*, 2011) for proper body functioning, whereas colour of food was reported to have a great influence on the choice of consumers (Pathare *et al.*, 2013).

For the Nigerian maize cultivars, WI and YI were used for the optimisation of roasting conditions. Total phenolics, total flavonoids, antioxidant activity, TEAA and TAA of the Nigerian maize cultivars were not considered for the optimisation process because they had R^2 <0.8 (0.26 – 0.75). The mean optimum roasting conditions (roasting temperature/rotating speed) of 189.9 ⁰C/90 Hz and 140.9 ⁰C/49.8 Hz were found for S28 (yellow kernel) and S33 (white kernel), respectively for the production of whole grain flour or meal with the best nutritional quality. Even though S28 and S33 are soft maize grains, their mean optimum roasting conditions differ significantly. This might possibly be due to the differences in colour and variety.

In addition to colour (WI, YI), TEAA and TAA were included for the optimisation of roasting conditions of the South African maize hybrids. The mean optimum roasting conditions for the production of whole grain flour or meal of H2G1 and H7D1 maize grains with the best nutritional

quality were found to be 185.0 ⁰C/65.5 Hz and 182.6 ⁰C/55.0 Hz, respectively. H2G1 and H7D1 hybrids are white hard maize grains and their mean optimum roasting conditions did not differ significantly, therefore, the average (183.8 ⁰C/60.3 Hz) would be considered as the recommended optimum.

Furthermore, the proximate composition, total phenolics, total flavonoids and free radical (ABTS, DPPH) scavenging capacity of whole grain flours produced using the optimised roasting conditions showed unaffected nutritional quality and better pasting properties (lower pasting temperatures and higher pasting viscosities) compared to the raw maize whole grain flours. Even though the roasted (optimally processed) and raw whole grain flours demonstrated better proximate composition and antioxidant properties than CMM, the pasting characteristics of the later were better. The better pasting properties of CMM in relation to that of the whole grain flours could be attributed the high dietary fiber (resistant starch) content of the later. Higher content of oil (which is unsaturated, containing ω-6 fatty acid) of the whole grain flours of the roasted maize (though not significant) is an indication of having lower keeping quality (shelf life). But, considering the health benefits of dietary fiber and unsaturated fatty acids to consumers, whole grain flours of the roasted maize varieties should be given more preference for consumption despite the possibility of having shorter shelf life compared to the raw and refined maize flours.

This study demonstrated that FCR could be a better alternative technique of roasting maize grains, compared to conventional (using dry heat) methods, for the production of whole grain flour due to its ability to prevent loss of nutrients, vitamins and antioxidant content and activity. The mean optimum roasting conditions 189.9 ⁰C/90 Hz, 140.9 ⁰C/49.8 Hz and 183.8 ⁰C/60.3 Hz could be applied for yellow soft, white soft and white hard maize grains, respectively for the production of high quality pregelatinised whole grain flours. Whole grain flours showed better nutritional quality and high potential of being used as a functional food ingredient. The low pasting viscosities and high pasting temperatures of whole grain flours, which result in the formation of a weaker gel at longer period compared to CMM flour, could be considered as a disadvantage. Investigation of shelf life and consumer acceptability of the whole grain flours of the roasted maize varieties is therefore recommended for further research. This will enable the provision of required keeping period of the whole grain flours for maintaining profitable and healthier production, marketing and consumption chain. Furthermore, two or more soft varieties each of white and yellow maize should be investigated to obtain statistically better optimum roasting conditions using the forced convection continuous tumble roaster. Milling industries should consider introducing the whole grain flour to consumers due its high yield (bran and germ not removed), enhanced nutritional values and ease of cooking. Since the whole grain flour is expected to have short shelf life, milling industries should regulate production with reference to rate of consumer purchase.

References

Bolade, M.K., Adeyemi, I.A. & Ogunsua, A.O. (2009). Influence of particle size fractions on the physicochemical properties of maize flour and textural characteristics of a maize-based nonfermented food gel. *International Journal of Food Science and Technology,* **44,** 646-655.

De Munter, J.S., Hu, F.B., Spiegelman, D., Franz, M. & Van Dam, R.M. (2007). Whole grain, bran, and germ intake and risk of type 2 diabetes: A prospective cohort study and systematic review. *PLoS Medicine,* **4,** 1385-1395.

Good, C.K., Holschuh, N., Albertson, A.M. & Eldridge, A.L. (2008). Whole grain consumption and body mass index in adult women: An analysis of nhanes 1999-2000 and the USDA pyramid servings database. *Journal of the American College of Nutrition,* **27,** 80-87.

Guan, X. & Yao, H. (2008). Optimization of viscozyme l-assisted extraction of oat bran protein using response surface methodology. *Food Chemistry,* **106,** 345-351.

Humpf, H.-U. & Voss, K.A. (2004). Effects of thermal food processing on the chemical structure and toxicity of fumonisin mycotoxins. *Molecular Nutrition and Food Research,* **48,** 255-269.

Jensen, M.K., Koh-Banerjee, P., Hu, F.B., Franz, M., Sampson, L., Grønbæk, M. & Rimm, E.B. (2004). Intakes of whole grains, bran, and germ and the risk of coronary heart disease in men. *The American Journal of Clinical Nutrition,* **80,** 1492-1499.

Jinap, S., Rosli, W., Russly, A. & Nordin, L. (1998). Effect of roasting time and temperature on volatile component profiles during nib roasting of cocoa beans (*Theobroma cacao*). *Journal of the Science of Food and Agriculture,* **77,** 441-448.

Lemos, M.R.B., Siqueira, E.M.D.A., Arruda, S.F. & Zambiazi, R.C. (2012). The effect of roasting on the phenolic compounds and antioxidant potential of baru nuts [*Dipteryx alata* Vog.]. *Food Research International,* **48,** 592-597.

O'neil, C.E., Nicklas, T.A., Zanovec, M. & Cho, S. (2010). Whole-grain consumption is associated with diet quality and nutrient intake in adults: The national health and nutrition examination survey, 1999-2004. *Journal of the American Dietetic Association,* **110,** 1461-1468.

Oboh, G., Ademiluyi, A.O. & Akindahunsi, A.A. (2010). The effect of roasting on the nutritional and antioxidant properties of yellow and white maize varieties. *International Journal of Food Science and Technology,* **45,** 1236-1242.

Oliviero, T., Capuano, E., CäMmerer, B. & Fogliano, V. (2008). Influence of roasting on the antioxidant activity and hmf formation of a cocoa bean model systems. *Journal of Agricultural and Food Chemistry,* **57,** 147-152.

Özdemir, M., Açkurt, F., Yildiz, M., Biringen, G., Gürcan, T. & Löker, M. (2001). Effect of roasting on some nutrients of hazelnuts (*Corylus avellena* L.). *Food Chemistry,* **73,** 185-190.

Özdemir, M. & Devres, O.Y. (1999). The thin layer drying characteristics of hazelnuts during roasting. *Journal of Food Engineering,* **42,** 225-233.

Pathare, P.B., Opara, U.L. & Al-Said, F.a.-J. (2013). Colour measurement and analysis in fresh and processed foods: A review. *Food and Bioprocess Technology,* **6,** 36-60.

Schatzkin, A., Mouw, T., Park, Y., Subar, A.F., Kipnis, V., Hollenbeck, A., Leitzmann, M.F. & Thompson, F.E. (2007). Dietary fiber and whole-grain consumption in relation to colorectal cancer in the NIH-AARP diet and health study. *The American Journal of Clinical Nutrition,* **85,** 1353-1360.

Westermann, C.M., Dorland, L., Wijnberg, I.D., De Sain-Van Der Velden, M.G.M., Van Breda, E., Barneveld, A., De Graaf-Roelfsema, E., Keizer, H.A. & Van Der Kolk, J.H. (2011). Amino acid profile during exercise and training in standardbreds. *Research in Veterinary Science,* **91,** 144-149.