1. INTRODUCTION

Corn (*Zea mays* L.), also known as maize, is heavily grown cereal crop throughout the world, after wheat and rice. According to United States Department of Agriculture data (USDA 2016), the annual worldwide production of corn was recorded to be 961.08 million metric tons in 2015/2016. In 2014, the estimated annual corn production in India has been recorded around 42.3 million metric tons (FAOSTAT 2014). On the basis of production, United States, China, Brazil, Europe, Argentina, Ukraine, India, Canada and Russia are main corn-producing countries. Corn yield in United States is the highest in terms of land planted and the net value. The economic value of corn has been raised due to its high yield that acts as metabolic energy source for animal feed and as sugar and starch source for industrial food products (McCann et al. 2007). In developed and developing countries with wide industrial era, corn is used in two ways; one as grains or fodder for animal feed and second as a raw material for production of starch, glucose, oil, high fructose corn syrup and extruded products through wet- or dry- milling processes (Tsaftaris 1995). The industrial demand of corn is increasing day by day due to its increased usage in production of ethanol and dried distiller’s grains (DDGs).

Corn is a widely consumed cereal that serves as nutritionally rich food with certain vitamins, essential fats, proteins and some macro and micronutrients (de la Parra et al. 2007; Nuss and Tanumihardjo 2010; Batal et al. 2010). Various mineral elements like copper, magnesium, phosphorus, potassium, zinc and calcium are present in corn and these plays an important role in human health for growth and regulation of bones, nerves and teeth, synthesis of hormones and enzymes as well as for cellular integrity, blood regulation and muscle contraction (Hambridge 2000). Whole corn grain is rich source of anthocyanins, flavonoids, carotenoids and phenolic compounds that provide potential health benefits to human (Zilic et al. 2012; Pandey et al. 2013). Anthocyanins impart red, blue and purple color to the corn grains (Giusti and Wrolstad 2003), while yellow and orange color of corn grains is due to carotene and xanthophyll pigments (de la Parra et al. 2007). In addition to color, the high antioxidant activity, anti-mutagenesis,
Introduction

anti-carcinogenesis and enzyme inactivation are certain health beneficial properties of these metabolites present in corn grain (Adom and Liu 2002).

Phenolic compounds are present in soluble ester, soluble free and insoluble bound forms in cereal grains (Liyana-Pathirana and Shahidi 2006; Zilic et al. 2012) that helps in prediction of the end-use suitability of cereal products (Naczk and Shahidi 2006). The high antioxidants activities are shown by phenolics that are concentrated mainly in the outermost layers of grains (Luthira and Liu 2013), along with certain other biological activities like DNA repair, cell differentiation, pro-carcinogen deactivation, estrogenic metabolism and induction of enzymes detoxification (Adom and Liu 2002; Shahidi 2004; Pandey et al. 2013). The polyphenols such as ferulic acid, p-coumaric acid and its derivatives present in white corn have antioxidant and anti-carcinogenic effect acquiring human health (Trombino et al. 2004; Del Pozo-Insfran et al. 2006). The coarse corn grain is considered to have higher phenolic content as compared to that from wheat, rice, oats and barley (Adom and Liu 2002; Ndolo and Beta 2014). The concentration of different phenolics like sinapic acid, ferulic acid, vanillic acid etc. varies in whole grain, germ, pericarp and endosperm of white and yellow corn (Chiremba et al. 2012; Das and Singh 2015).

Kernel of corn grain is consisted of three major parts: germ (embryo), endosperm and pericarp (hull or bran) (Watson 2003). The milling of corn grain is done to obtain these fractions, each of which is utilized for different purposes. Endosperm is processed into variety of food and feed products for human, animal and livestock consumption, bran is utilized for animal feed and germ is used for corn oil extraction (Burger et al. 2013). Germ portion of corn grain constitutes high crude lipid content, high minerals and proteins (Zilic et al. 2011), while pericarp contains high crude fiber content (Burger and Duensing 1989). Corn of different types viz. dent, flint, floury, waxy, popcorn and sweetcorn is grown, each type has different proportions of horny (vitreous) and floury endosperm (Knott et al. 1995). Dent corn (Zea mays var. indentata) is differentiated with a depressed crown (due to soft floury endosperm). Flint corn (Zea mays var. indentata) is also named as Indian corn with a hard outer shell and central soft starch portion. Floury corn, also named as “soft” corn where major
proportion of soft endosperm with a small portion of hard endosperm is present (Singh et al. 2011a).

Dry milling of corn grains produces grits and flours of different particle size that are further processed for breakfast cereals, snacks and extruded or cooked products (Lee et al. 2006; Singh et al. 2014a). The major emphasis of dry milling industries is to separate the endosperm from germ and pericarp with maximum grit and flour yields along with the purity of products, by consuming minimum energy. Wet milling of corn generates starch, gluten meal, oil, germ meal and steep liquor as end products, among which, starch is the chief constituent of wet milling industry (Hespell 1998). The variation in grain hardness is a remarkable grain quality aspect that plays a central role in the extraction and processing of cereal grains and in end-use quality of grain products (Shandera et al. 1997; Bettge and Morris 2000). Food industries dealing with dry milling and alkaline processing of corn prefers the hard and large grains with easily separable germ and pericarp during the process (Wu 1992). On the other hand, wet milling industries prefer soft corn grain, which usually requires less drenching and leads to good separation of starch and proteins (Chandrashekar and Mazhar 1999).

The corn grain proteins are studied as a class of zein that contributes largely to the variation in grain hardness (Robutti et al. 1997). Zeins are the alcohol soluble, low molecular weight seed storage proteins in corn (Lending and Larkins 1989). Zein protein content varies among different parts of corn grain (Singh et al. 2012) and the behavior of corn zein is highly dependent upon the type of endosperm (Larkins et al. 1989).

The corn starch yield and purity is highly influenced by the variation among corn cultivars and wet milling conditions used for isolation of starch (Nerying and Reilly 1984). Corn starch is widely used as a gelling agent, thickener, bulking agent and water retention agent in food industry (Singh et al. 2003; Eliasson and Gudmundsson 2006). Starch is present in plants as semi crystalline granules and comprised of linear amylose and branched amylopectin chains (Gallant et al. 1997; Garcia-Alonso et al. 1999) and corn is categorized as normal, waxy and high amylose corn on the basis of amylose to amylopectin ratio (Sandhu and Singh 2007). Waxy corn starch is mainly composed of amylopectin (~99 %) and a very less amount of amylose (~1 %) is present.
The structure, composition, distribution and granular packing of amylose and amylopectin depend upon the origin of starches (Kurakake et al. 2009). Amylose content and amylopectin branch chain length plays a central role in determining the pasting properties of corn starches (Tziotis et al. 2005). Starch gelatinization determines the thickening and swelling characteristics of starches for their potential use in food industry as thickener (Karim et al. 2007). The porosity of corn starch granules is studied using microscopic techniques (Fannon et al. 1992; Sujka and Jamroz 2009) and this porous structure facilitates the diffusion of enzymes (Dhital et al. 2010), proteins, peptides and volatile compounds (Zeller et al. 1999) with impact on texture and mechanical properties (Rahman 2001). The high crystallinity of waxy corn starch granules is related to the amylopectin branch chain length that is different for normal corn starches (Singh et al. 2006a). The distinct behavior of waxy starches increases their demand as stabilizer in food industry and as adhesive in paper industry (Ptaszek et al. 2009).

Snack foods have become a fundamental part of the eating habits of majority of the world's population. The consumption and demand of shelf stable and ready-to-eat foods has increased and the fabrication of such products is done by various methods. A well-established thermal technique used for processing of corn is extrusion cooking with unique feature of higher productivity in very short time (Morsy et al. 2015). Corn grit obtained during dry milling is a major ingredient of commercial extruded foods with good expansion characteristics (Singh et al. 2009a). Extrusion behavior and product properties are significantly influenced by extrusion variables, feed material and particle size distribution (Singh et al. 1998a; 1998b). The blending of corn with other cereals, pulses and gums gives the extrudates with enhanced nutritional value, more puffing, crispiness, expansion and flavor (Seth et al. 2015; Liu et al. 2000). The crunchy texture, porous structure, more expansion, appealing mouthfeel and flavor of extrudates are major characteristics that influence consumer acceptance and preference (Kasprzak et al. 2013).

Corn based products are seeking demand as a gluten free alternative stuffs due to high prevalence of gluten sensitivity or celiac disease (Fasano et al. 2003; Torbica et al. 2010). Corn chapatti is a good substitute as gluten free diet which is consumed as a
Introduction

Staple food in Indian subcontinents, especially in north India. Although, corn flour is found less acceptable for baked products due to lack of storage proteins exhibiting viscoelasticity in dough (Shewry et al. 2002), but certain modifications like warm water for dough preparation, long time of dough kneading may help in enhancing the dough elasticity (Singh et al. 2011b).

The optimum dough development requires optimal water and mixing conditions. The mixing behavior of dough can be predicted using rheological testing that provides certain information to predict the quality of final product (Dobraszczyk and Morgenstern 2003; Rosell et al. 2007; Moreira et al. 2010). The protein secondary structure analysis can be used to relate the rheological behavior of developing dough directly to the changes in structure of proteins (Seabourn et al. 2008). Fourier transform infrared (FTIR) spectroscopy is a well-established technique for determining the protein secondary structure and chemical microstructure of foods (Wetzel and Reffner 1993).

Various studies on physicochemical properties of corn grain and starches have been explained in literature. The role of certain phenolics present in corn and their relationship with antioxidant activity and human health has also been studied but the literature related to the distribution of phenolics in corn fractions is limited. The literature directed that in depth study has not been conducted to compare the dry milling behavior of normal and waxy corn and composition and protein profile of their fractions. Moreover, the effect of using waxy corn in extrusion and its effect on certain properties of normal corn processing has not been extensively explained. Although, the impact of temperature and time on dough making and dynamic rheological properties of corn has been explained previously, literature studying the comparison of varied water levels with mixing, rheology and protein secondary structure of corn meal along with the role of waxy corn meal is limited.

Thus, the present study was framed to achieve the following objectives:

1. To evaluate physico-chemical and protein characteristics of grains from corn germplasm.

2. To compare the phenolic profile of whole grain, flour and bran from different corn varieties.
Introduction

3. To study physicochemical, pasting and protein characteristics of grit and flour fractions obtained from dry milling of selected corn varieties.

4. To evaluate structural and functional properties of starches isolated from selected corn varieties.

5. To study the extrusion cooking and chapatti behavior of selected corn varieties.