REVIEW OF LITERATURE
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2.1. Cereal Starches and Fractions

Starch is the major constituent of grains as well as the greatest source of energy in human diet. Though cereals do not differ much in their starch content normally having (70-80%), the nature of starch and inturn its digestibility play a major role in its rate of absorption.

Englyst et al (1992) classified starch for nutritional purposes into rapidly digestible starch (RDS), slowly digestible starch (SDS) and resistant starch (RS) as well as RS further three fractions such as RS$_1$, RS$_2$, and RS$_3$ and recommended the method for determination of starch fractions in different foods by controlled enzymatic hydrolysis with pancreatin $\alpha$-amylase and amyloglucosidase.

Englyst and Hudson (1996) studied the starch fractions in cereals, legumes, cereal products and tubers. Resistant starch was found to be higher and RDS lower in legumes, may be due to encapsulation of starch by cell walls (dietary fiber and protein). They explained that rate and extent of starch digestion in humans could be modified through food processing benefiting both the consumer and food industry. RDS in rye bread was higher than wheat and corn breads while RS was significantly high in wheat bran bread (Tass and EL-SN 2000). Starch digestibility index have been found to negatively correlate with RS content for the breads. Sharavathy et al (2001) studied the rate and extent of starch digestion in-vitro in ten Indian foods.
based on cereals. The result indicated that the starch hydrolysis differed in foods due to raw ingredients used, pre-processing treatments applied, time and type of processing adopted as well as the addition of accompaniment with the product. Thus they concluded that the specific health benefit could be related only when various types of starches i.e. digestible, slowly digestible and resistant in foods were measured. Arthi et al (2003) studied the in-vitro starch digestion in rice, ragi, wheat, jowar and their blends. The results indicated that the amylose influenced the rate of starch digestion and reflected on the blending proportion of cereals. They also reported that the measurement of starch fractions in foods might help in the identification of specific health benefits.

Effect of de-branching time, storage time, and structural properties of slowly digestible starch (SDS) from waxy sorghum were investigated by Shin et al (2004). The DSC studies indicated that sorghum hydrolysed by $\alpha$-amylase for 9 hr and 16 hr resulted in SDS and RS respectively. However, the residue after 9 hr incubation consisted of less perfect crystallites and amorphous components.

2.2. Thermal Properties

Starch being the major component of millet, gelatinisation is one of the main transition phases occurring during processing of millet and millet products. The thermal properties of flours and starches play an important role in product development. Fujit et al (1996) studied physico-chemical
properties of starch from foxtail millet using DSC. The results indicated a positive correlation between peak temperature and enthalpy changes.

The thermal properties of maize starches during product development were studied by NG, et al (1997) using DSC. They reported that a starch with desired thermal properties might be obtained by appropriate selection of endosperm genotype and stage of maturity during harvesting. Thermal behavior of dry native starch, amylase and amylopectin was investigated using thermogravimetry (TG) and DSC by Zhiqiang et al (1999). The decomposition temperature of dry native starch, amylase and amylopectin increased with the molecular weight of the specimens. The thermal properties of flour from 12 varieties of cowpea were studied using DSC by Henshaw et al (2003). They reported that the DSC parameters such as transition, onset and peak temperatures as well as enthalpy varied significantly among the varieties.

Physico-chemical properties of starches from 12 different potato varieties were investigated by Yusuf et al (2003) with respect to the gelatinisation characteristics of the starches. The influence of variation between the cultivars was much less apparent than the influence of environmental temperature. Aggarwal et al (2004) studied the morphological and thermal properties of starches isolated from pea cultivars. They concluded that the starch with the highest enthalpy may be due to the presence of many large-size and irregular granules and the pea starch, which showed the lowest enthalpy, contained small size oval granules. Noda et al
(2004) studied the effect of harvest dates on the properties of potato starch. Environmental temperature clearly increased the gelatinisation temperature and enthalpy as measured by DSC. Peak viscosity and breakdown were higher in case of late harvest than the early one.

Premavalli et al (2005) studied the phase transition behaviour of finger millet (ragi) starch at different moisture levels using DSC. The effect of annealing, quenching on ragi flour and its components were also studied. The peak gelatinisation was observed at 1:3 (starch-water) ratio with the gelatinisation temperature of 78°C. The quenching and annealing processes decreased the gelatinisation temperature (GT). The GT of ragi flour and mixture of starch, protein and fiber were higher than that of the starch alone, indicating that the additives increased the GT of ragi starch.

Pasting properties and amylose contents of various types of polished rice were analysed and compared by Yang et al (2001) and reported that significant differences existed in amylose content, pasting curves and viscosity characteristics between rice type. Mohan et al (2005) have reported higher peak viscosity for ragi compared to rice starch.

2.3. Functional Properties

Resistant Starch: Finger millet being a nutritionally strengthful cereal has a number of functional properties such as slowly digestible starch fraction, which helps for diabetics, resistant starch fraction, a functional fiber and digestibility characteristics and high dietary fiber. The measurement of
resistant starch is quite laborious and several factors affect its determination. Therefore several workers have contributed to the methodology of RS determination and modified suitably.

**Calixto et al (1993)** modified the method for measuring resistant starch (RS) in dietary fiber residues. This procedure had the limitation of quantifying RS in foods without determining fiber. A simple method for resistant starch (RS) determination in food and food products has been proposed by **Goni et al (1996)**. The modification included the removal of protein and digestible starch as well as solubilisation and enzymatic hydrolysis of RS and quantification of RS as free glucose released. **Ranhotra et al (1996)** evaluated the energy value of RS in rats and suggested that it provided no energy. Thus could be used in low calorie foods. **Ring et al (1988)** have also reported that RS can be used as a low energy bulking agent in the development of foods.

**Gelroth and Ranhotra(2000)** developed a modified method for RS. RS was determined in 70 grain based foods by modification of the method used to measure total dietary fiber. The modification involved solubilising RS in dimethy sulphoxide (DMSO) and the difference between with and without DMSO gives the RS content. Bread products and breakfast cereals contained over one – third of the total dietary fiber as RS.

The processing methods affected the resistant starch retention / formation thereby influencing the functionality of the products. The
development in the various types of processed foods, with specific health benefits needs more basic information on the active components.

Piatel and shurpalekar (1994) studied RS content and effect of processing on RS in selected cereals (rice, ragi, sorghum, and wheat), legumes (red gram dhal, bengal and green gram whole and dhal) and vegetables (potato, yam, tapioca, sweet potato, colocasia and green plantain). Higher RS was found in foods subjected to dry heat treatment as compared to wet processing. The RS of rice and amaranth starch subjected to processing treatments have been reported by Prachure and Kulkarni (1997). Processing treatments such as pressure cooking and cooking resulted in increase in RS and frying decreased.

Experiments were conducted by Skrabanja and Kreft (1998) to investigate the extent of changes in buckwheat starch and starch components that can occur during autoclaving. Autoclaving and cooling cycles did not affect the proportions of SDS or RS in buckwheat. But significant rise in retrograded starch (RS3) was observed.

The Effect of processing and storage on RS in foods was studied by Kavitha et al (1998). Studies indicated that RS content of freshly gelatinized samples of corn, wheat, ragi, rice, sago and potato flours increased on low temperature storage after 24 and 48hr and decreased on reheating. The fermented samples such as idli and dhokla had lower RS content. Namratha et al (2002) reported that RS increases on storage in ready to eat foods.
They have concluded that in addition to processing methods used, duration of storage could be an important factor, affecting RS formation in RTE foods. During storage the dispersed polymers of gelatinised starch are said to undergo retrogradation to semi crystalline forms that resist amylolytic digestion.

Mangala et al (1999c) reported that the defatting and deprotenisation increased the recovery of RS. The RS content in processed rice and ragi has been reported by Mangala et al (1999a). They have reported that RS increased during repeated autoclaving-cooling cycles. The content of RS of rice was higher than that of ragi.

**Starch Digestibility:** Digestion of starch begins in the mouth with the reaction of salivary α- amylase, but the hydrolysis stops in the stomach because of changes in pH and later, it is resumed in the duodenum where pancreatic α- amylase is secreted. The rate of starch digestion is affected by the physical form of food – its shape, crystallinity of the starch granule, recrystallisation and retrogradation characteristics, amylose-lipid complexes, native α- amylase inhibitors and other factors.

Effect of different processing treatments on *in-vitro* starch digestion rate and RS formation in moth beans as well as horse gram was studied by Bravo et al (1998). Sprouting and direct cooking resulted in the lowest RS, while soaking significantly improved the starch digestibility. Urooj and Puttraj (1999) studied the rate of starch hydrolysis in 10 cereal based food
preparations such as chapathi, dosa, idli, pongal, poori, ragi roti, rice flakes, rice roti, semolina idly and upma. In- vitro starch digestibility was found to be the lowest in chapathi and highest for rice flakes. They reported that the use of carbohydrate rich foods in therapeutic diets could be related to their in-vitro digestion characteristics.

Elmoneimo et al (1999) reported that in-vitro starch digestibility of sorghum increased in presence of cystein, sodium metabisulphate or ascorbic acid. They also reported an increase in gelatinisation temperature as well as peak and breakdown viscosities. Devi and Geervani (2000) reported higher in-vitro starch digestibility for puffed, boiled and par-boiled rice than in raw rice. The effect of processing on the in-vitro protein and starch digestibility, non starch polysaccharides and RS in three varieties of rice as studied by Sagum and Arcot (2000), concluded that both boiling and pressure cooking significantly increased the level of readily digestible starch while decreasing the slowly digestible starch and RS which in turn increased the starch digestibility. The influence of domestic cooking on RS and in-vitro digestibility of potato starch had been studied by Garcia and Goni (2002). Domestic cooking decreased RS content and increased the digestibility of boiled and mashed potatoes when compared to raw potatoes. Frie et al (2003) studied the starch hydrolysis and glycemic index in six rice cultivars differing in amylose content. The results indicated that the amylose content as well as treatment had an impact on the starch digestibility. Cooking and storage of rice in refrigerator lead to a reduction in glycemic index for all the cultivars.
Physiological Benefits of Fiber and Functional Fiber: As a functional fiber, RS is white in colour and its fine particles and bland taste make it possible to be a part of a variety of food products that have better consumer appeal and greater palatability than those made solely using the traditional fiber. Thus, RS not only fortifies fiber but also imparts special characteristics and physiological benefits compared with those of high fiber foods.

Navita and Sumathi (1992) studied the effect of processing on dietary fiber content in ragi, bajra, sorghum bran and wheat bran. The insoluble fiber content of unprocessed and processed flour samples was found to be high in ragi and a significant decrease in total dietary fiber in all the samples was observed on processing.

Chemically RS from maize and pea starch were prepared and fed to the rats. The animal studies indicated that pea RS was almost incompletely digestible in small intestine and 50% in maize RS (Annison and Topping 1994). The influence of nutrients and other food constituents such as dietary fiber, catechin and phytic acid on RS formation was studied by Escarpa et al (1997). All the food constituents decreased the formation of functional fiber RS. Tuley (2000) has explained that RS can be used to exchange dietary fiber contents of baked snacks without affecting texture and development of an alternative adhesive system to fats and oils. Yue and Waring (1999) discussed the food applications of RS and reported that breads containing RS had superior quality compared to the traditional fibers. They explained that RS as an ingredient imparted crispiness to foods such as crackers, waffles as
well as French toast and its expansion ability could be used to impart unique
textural properties to cereals and snacks.

Ring et al (1988) explained that RS present in a food will help to flatten
the glycemic response curve by reducing the amount of rapidly digestible
starch and moderating the rate of digestion. The slow release carbohydrate
finds their application in improving the carbohydrate tolerance in diabetes.
Yue and Waring (1999) explained the physiological benefits of RS, along with
its functional properties. They explained that by formulating foods with RS,
researchers can encourage consumers to increase the fiber intake.

Wepner et al (1999) explained that RS possess similar physiological
features as these of dietary fiber and could be used to enrich the foods. They
also studied chemical modification of native starch of wheat, pea, corn and
potato using citric acid and used the same in product development such as
toast, bread, pasta and extrudates.

Woo and Seib (2002) studied the effect of phosphorylation of wheat,
corn, oat, rice, tapioca, mung bean, banana and potato starches as well as
formation of cross-linked RS4. The RS4 starches showed low swelling powers
and no pasting curves. They found that RS4 had increased transition
enthalpies than their native counterparts. This may be due to the fact that
cross-linking could inhibit melting of crystals in starches granules. Brouns et
al (2002) explained that RS on fermentation in intestinal flora lead to the
formation of propionate and butyrate, which helped in the maintenance of gut
health and the reduction in risk of colorectal cancer.

2.4. Interaction of Starch with Major Nutrients

Starch, proteins and lipids are the major components in cereal based
food products. The interactions among these components lead to the
formation of complex which in turn altered the functional and thermal
properties of cereals which affected the food system.

Lorenz and Hinze (1976) studied the functional characteristics of
porso and foxtail millets and compared the same with wheat and rye starches.
The millet starches showed higher water binding capacity and gelatinisation
temperatures than these for wheat starch. Solubility of the millet starches was
lower than that of wheat starch. Chandrashekar and Kirlesis (1988) studied
the influence of protein on starch gelatinisation in nine varieties of sorghum. It
was observed that hard (varieties) grains produced thinner, less sticky gels
than soft grains. Acid gels were thinner than the alkali gels i.e. involvement of
protein in limiting starch gelatinisation in hard sorghum and there by
producing thinner gels.

Sievert and Pomeranz (1989) investigated the formation of RS from
wheat, maize, potatoes, pea, waxy maize and amylo maize. Formation of RS
was characterized by three different techniques such as enzymatic assay,
DSC and SEM indicating that RS was derived mainly from recrystallised
amylose. DSC data revealed that amylose-lipid complexes were not involved
in the formation of RS. Gidshall and Solms (1992) reported that an
important source of interaction involved the amylose portion of starch, which had the ability to form helical structures around the molecules. The amylopectin had a little tendency to form complexes. They also reported that ungelatinised granules would take up water, methanol, ethanol, 1-propanol and 1-butanol.

Starch-lipid interactions and formation of RS in high-amylose barley was studied by Szczodrak and Pomeranz (1992). Barley starch interacted with monoglycerides and formed amylose-lipid complexes indicated by peaks in DSC thermograms at temperature in the range of 100-112°C. Endothermic transition at 158°C reflected the presence of crystallized amylose. RS yield for single autoclave and cooling cycle was 7.1g which decreased to 0.7-5.3g in the presence of different emulsifiers. Studies indicated that amylose crystallization involved in the formation of RS was affected by various emulsifiers.

Chel et al (1993) has reported on the chemically modified rice’s by treating with propylene oxide and hydroxypropylation. Hydroxypropylation of rice caused an extreme decrease in gelatinisation temperature from 62°C to 50°C and reduced the retrogradation rate of cooked rice.

The interaction between waxy cornstarch and monoglyceride was investigated by the measurement of starch-monoglyceride complex formation, iodine affinity, DSC and texture measurements by Huang and
White (1993). Interaction decreased the iodine affinity and gelatinisation onset temperatures.

Wannerberger and Eliasson (1993) studied the thermal behaviour of rye flour-milling streams and the results showed that the levels of protein and damage starch showed a double endotherm. They concluded that the milling process affected the interaction between crystalline regions and the amorphous parts in the starch granules. The gelatinisation behavior of starch is known to depend not only on the water content but also on other components such as sugar, salt, polar lipids and fats. Proteins affect the starch gelatinisation because water separates into two phases: a protein aggregate phase and a starch phase. Gelatinisation behaviour of starch was different from that of flour. Increased level of damaged starch increased the gelatinisation onset temperature ($T_o$), peak maximum temperature ($T_m$) and enthalpy ($\Delta H$).

Lipid-protein and lipid-starch interactions during extrusion of a soy protein isolate and rice flour blend were evaluated by Chu (1995). The studies showed that moisture content of feed was the main factor affecting interaction of lipids with the other food components. At 200°C and 13% moisture content, due to protein denaturation and starch gelatinisation, interaction between lipid and starch became predominant. Interactions varied according to the lipid class.
Erdogdu et al (1995) studied the interaction patterns of dairy fractions (acids and sweet whey and casein) and flour components using DSC. The studies indicated that lactose and whey interacted with starches and gluten and in turn increased the gelatinisation temperature and enthalpy where as casein did not have any interaction.

Amylose-lipid complex formation in acetylated pea starch-lipid system was studied by DSC while the measurements of iodine affinity by Hua-Liu et al (1997). DSC thermal curves of gelatinised modified pea starch containing fatty acids or monoglyceride did not show DSC transitions indicative of amylose complexes with external lipids, where as DSC endotherm of amylose-lipid complexes was observed for native starch-lipid. Iodine binding affinity studies revealed that the acetylated pea starch amylose complexed with added fatty acids or monoglycerides.

Starch-lipid interactions in four maize genotypes with four surfactants were studied by Villwock et al (1999). The ionic surfactants with $C_{12}$ hydrocarbon tail reduced the gelatinisation onset temperature, while it did not occur in case of neutral or long chain hydrocarbon surfactants. Marson and Topping (1999) have concluded that increase in rice particle size increased escape of starch digestion in small intestine. Vazquez et al (2003) studied the interaction of granular maize starch with polar lipid using DSC. The results indicated that in the absence of lysolecithin the crystallization occurred at 80-95°C, while in presence of 1.86/3.35% lipid concentration it increased to
130°C, indicating the lipid-amylose interaction in starch granules. Rheological properties of corn and waxy corn starch pastes were analysed, and effects of lipid addition on swelling capacity of starch granules and amount of amylose leached from the granule during heating were studied in corn, wheat and waxy corn starch system by Navarro et al (1996).

Ryu and Walker (1993) have studied the pasting properties in wheat flour. They have reported that the decrease in peak viscosity and increase in breakdown viscosity with the addition of emulsifiers and can be explained by the presence of amylase-emulsifier complexes, because coating the starch surface delayed water transport into the starch granule, and thus decreased swelling. Fitzgerald et al (2003) have explained the starch lipid complex in rice altered the viscosity curves. The reduction in viscosity by the oils depends upon their ability to form complexes with starch (Singh et al 2000). Zhang and Hamaker (2003) reported that fatty acids alone with sorghum starch produced an increase in starch pasting viscosity at the cooling stage.

2.5. Structural Characteristics

The granule morphology of the starches can be studied by scanning electron microscope (SEM). The morphology and crystallinity of sweet potato was studied by Asante et al (1993) and observed a mixture of rounded and angular granules, while smoother surfaces for rounded granules. The variation in size and shape may be due a difference in biological origin. The SEM of starch samples separated from different pea cultivars have been reported by Aggarwal et al (2004). The SEM examination of the native,
cooked and enzyme treated ragi starch have reported by Mohan et al (2005) and found that cooking or enzyme digestion leads to complete loss of starch granular structure. They have also reported that high degree of fragmentation in rice starch but only a few bigger chunks in case of ragi starch.

Roopa et al (1998) have studied the SEM analysis in ragi based preparations and reported a complete disintegration of starch granule in dumpling, which could be related to a 100% gelatinisation. The deep fissures in the starch granules have been reported to be indicative of a strong bond between the starch and the protein matrix (Colonna et al 1980). The morphology of starch granules depends on the biochemistry of the chloroplast or amyloplast, as well as physiology of the plant (Badenuizen 1969). Bhatnagar and Lincon (1997) have reported that native corn starch showed individual starch granule with definite shape and size without rupture, while extrusion of starch resulted in complete disappearance of the individual intact starch granules. They have also reported that with the addition of lipids prior to extrusion, structure was further modified.

The crystalline properties of starch granules can be studied using x-ray diffraction. X-ray crystallography study has been reported in 6 varieties of isolated ragi starch by Samantaray and Samantaray (1997) and reported that the size of the crystalline regions was related to the sharpness of the diffraction profiles. The x-ray diffraction peaks were sharp for samples, containing large crystallites and extent of crystallinity and size of the crystalline regions vary. Cheetham and Tao (1998) have studied the
variation in crystalline type with amylose content in maize starch granules. 

Gernat et al (1993) reported that wheat and maize starch showed an A-type, while pea starch showed B-type diffraction. Mangala et al (1999b) reported that autoclaving of aqueous ragi flour suspension increases the RS content. GC-MS analysis revealed that RS is a linear molecule. X-ray diffraction data showed that ragi RS have both B and V-type diffraction patterns. Thermal behavior of starch evaluated by DSC revealed that RS endothermic peak starts at around 100°C and constituents of ragi flour, such as protein, lipids and non-starchy polysaccharides do have a lowering effect on the gelatinisation temperature and enthalpy values of starch.

Mohan et al (2005) have reported that enzymatically hydrolysed ragi starch had higher degree of crystallinity as compared to the rice starch. They have also reported that the crystallinity of the residues from enzymatically hydrolysed ragi starch was significantly higher than rice starch residues. The crystallinity of starch samples isolated from wheat grains and then subjected to freeze drying, vacuum oven drying or air drying have been measured by Ahmed et al 1978. They have reported that freeze drying maintains the starch in its original form with the other methods an increase in polymer order occurs.

The literature on starch fractions is very much limited in case of basic materials while in some processed foods, it has been extensively reported. The studies on gelatinisation behaviour of starches as measured by DSC revealed that studies on ragi starch were almost non-existing except the
enzymatically hydrolysed ragi starch by Mohan et al. (2005) and comparison of ragi and rice starch properties by Mangala et al. (1999). The functional characteristics of cereals, which have a direct impact on the benefits to consumers, have been studied from different angles and the reports specifically on finger millet and their products remain open for research. However, a few comparative reports on the effect of processing on resistant starch and its digestibility in cereals revealed differential behaviour of wheat, rice and ragi. The interaction of starch with lipids or proteins resulted in changed behaviour in terms of starch characteristics but needed a deeper understanding of the mechanisms.