__Review Article__

Millets starch – a potential functional ingredient

Abstract

Millets are primitive grains that were majorly cultivated in Indian subcontinent from ancient times. Theses are small seeded categorized as major and minor millets. Millets are resilient to adverse effects of climate change. They are regarded as "nutri-cereal" due to their high nutritional value compared to rice, wheat, and corn. Starch is the major nutritional constituent of millets with average content ranging from 55% to 61% in different millets. The application of millets depends on the physicochemical, structural, and functional properties of their starch. Millet starch is majorly isolated by wet milling methods, however, studies have shown the effect of dry milling on structural and functional properties of millet starches. Moreover,non-thermal methods have also been employed to enhance the functionality of millet starches. Studies have also demonstrated the functionality of millets in improvement of human metabolic heath and life-style related diseases. Modified millet starches are also utilised in food and non-food industries.

Key words: functional food, millets, nutri-cereals, resistant starch, starch, starch extraction

1. Introduction

Millets are primitive crops which are the part of Indian subcontinent cropping system since 3000 BC (Pokharia*et al*., 2014). These are small seeded grains belonging to Chlorideae and Paniceae tribes of the Poaceae family. Millets are broadly categorized as major and minor milletsbased on their availability and verity(ICRISAT 2017). Major millets include sorghum, pearl (*Pennisetum glaucum*), finger (*Eleusine coracan*), foxtail (*Seratiaitalica*) while,proso (*Panicum miliaceum*, barnyard (*Echinochloacolane*), little (*Panicum miliare*), and kodo (*Paspalum scrobiculatum*) are classified as minormillets. They are regarded as climate smart crops due to their short cultivation period, less water requirement, high adaptability towards adverse climatic conditions, and better productivity on the marginal lands than the major cereal crops (Bandyopadhyay *et al*., 2017).

Millets are considered as "Nutri-cereal" because of their high nutritional and nutraceutical value compared to rice, wheat and corn (Government of India, 2018). Millets contain 60–70% carbohydrates, 1.5–5% fat, 6–19% protein, 12–20% dietary fiber, and 2–4% minerals. Moreover, millets are rich source of B complex vitamins, lipids, dietary fiber and polyphenols (Ambati & Sucharitha, 2019). The high worldwide demand and acceptance of millets is owing to its gluten free property which makes millets suitable for consumption by people suffering from celiac disease. Additionally, epidemiological studies provide evidences of health promoting and metabolic effects of millet consumption(Anitha *et al*., 2021). Starch is the most abundant storage polysaccharide in plants and is the major component of diet.More than half of total energy supply to human body is contributed by starch rich grains. In case of millets, starch majorly (more than 50%)contributes to total nutritional constituents of grains. The application of millets for foods and other purposes significantly depends upon the physicochemical, structural, and functional properties of their starch (Mahajan *et al*., 2021). The starch is classified as rapidly digestible starch (RDS), slowly digestible starch

(SDS), and resistant starch (RS) based on the action of amylases on them and time taken for digestion in the small intestine. The RDS and SDS fraction is hydrolysed to glucose in small intestine, while, the RS fraction is resistant towards enzymatic hydrolysis in stomach and small intestine and fermented by large intestine microbiome (Meenu & Xu, 2019). So resistant starch may also be considered as source of dietary fiber.

2. Millet Starches – composition

The average starch content of pearl, finger, foxtail, proso, barnyard, little, kodo millets ranges from 55-65%, 53-68%, 57-73%, 58-78%, 48-60%, 43-58%, 46-61% respectively (Kaimal *et al.*, 2021). In addition to differences in the starch content amylose contentalso varies in different millets ranging from 13-18% in pearl and finger millets and 1.38-12.35%, 2.24-38.67, 8.90-18.5, 11.9-18%, 15-18% in foxtail, proso, barnyard, little, and kodo millet respectively(Prasad & Sahu, 2023). Furthermore, the average content of resistant starch also differs as 1.89-2%, 9-17%, 35-51%, 8-19%, 40-45%, 45-47%, 37-52% in finger, pearl, foxtail, proso, barnyard, little, and kodo millet respectively (Bora *et al.*, 2019). Studies have reported average glycaemic index of major and minor millets as 49-54, 41-54 respectively, whereas that of wheat and rice were observed as 64 and 83 respectively (Sharma & Gujral, 2020). Moreover, SEM micrographs revealed polygonal and round shape of pearl millet starch with a A-type structural pattern (Aruna & Parimalavalli, 2022). A study conducted on different varieties of foxtail millet revealed differences in amylose content from 12.3% to 27.4%. The amylose content was found negatively correlated to ordered double helical structure and crystallinity. The shape of foxtail millet starch was found polygonal, spherical. Furthermore, the decreased amylose limited the swelling degree of starch granules and in turn decreased the characteristic viscosity (Shi*et al.*, 2023).In another study slowly digestible starch and resistant starch content from estimated 43.38% - 49.15% &3.75% - 4.58% respectively in different varieties of finger millet grown in Sri Lanka. Moreover, the finger millet varieties were found excellent source of sources of dietary fibers when compared to commonly consumed cereals such as rice and wheat (Jayawardana *et al*., 2019).

3. **Millet Starches – extraction**

In the matrix of millet grain, the starch molecule has been found closely enclosed with the protein granules. Different chemical and enzymatic methods have been employed to solubilize the protein fraction and obtain starch molecules from the millet grain matrix (Verma *et al*., 2018; Halal *et al*., 2019). The extraction of starch encompasses three successive steps i.e. fragmentation of starch granules, breakage of starch followed by purification of starch. The starches are extracted by wet milling method. In wet milling the millet grain flour is steeped into different mediums viz. neutral (aqueous), acidic, and alkaline followed by steeping in antimicrobial salt solution. The steeping facilitates fragmentation and isolation of starch from the grain flour. After steeping the isolated starch is washed followed by centrifugation to remove undissolved impurities. The sediment layer obtained after centrifugation is collectedand dried (air drying/freeze drying) to obtain native starch(Kanagaraj*et al*., 2019). In case of resistant starch, RS_1 and RS_2 fractions are inherent to the millet grain (Kaimal *et al*., 2021). Whereas, the commercial RS_3 and RS_4 content of resistant starch can be prepared by modification through thermal, chemical, and bio-chemicalmethods, microwave and ultrasonic techniques and combination methods (Zheng *et al*., 2020). In a study conducted by Aruna & Parimalavalli, (2022) isolation of pearl millet starch was done by three methods basedon sodium azide, mercuric chloride, and sodium metabisulfite with lactic acid respectively. The highest yield of starch was obtained in case of acid extraction method. The starch isolated by acid had higher amylose content, swelling power, and functional properties. In a different approach, Gautam *et al*., (2021) isolated finger millet starch by alkali soaking method. In this method finger millet grains were cleaned and soaked in sodium hydroxide solution (0.25%) at 15 °C for 24 h followed by grinding of grains and decantation of starch. Isolated starch was washed and dried at 35 °C for 24 h. In another study Li *et al.*, (2020) extracted starch from millet grains by soaking them in 0.2% sodium hydroxide solution for 12 h at 25 °C.However, some studies have suggested use of dry milling techniques like dry fractionation and electrostatic separation as wet milling is commonly involves harsh processing conditions. Moreover, a solvent-free, dry approach has been found to preserve the native structure and function of plant macromolecules (Kuspangaliyeva*et al.*, 2023) andhence, present an alternative option for the enrichment of starch and fiber in plant foods(Assatory*et al.*, 2019). Moreover, in order to improve extraction, functional and physicochemical characteristics of native starch Mirzababaee et al., (2022) employed high hydrostatic pressure on millet grains. The grains were pressurized at200, 400 and 600 MPa for 10, 20 and 30 min. All the treatment resulted in decreased swelling strength and solubility of millet starch, however, water holding capacity of the starch increased. Thermal analysis showed a decrease in gelatinization temperature and enthalpy of gelatinization and the pasting properties showed a decrease in the peak viscosity after treatment. Moreover, hydration, surface area, & porosity of the millet starch increased after high pressure treatment and led to an increase in the elastic nature of the starch samples. So high pressure processing can be used as a green technology to improve properties and enhancement of utilization of starch in industries (Mirzababaee*et al.*, 2022).

4. Millet Starches – therapeutic role

The millet starches can be used as prebiotic food for the growth of healthy microflora in human gut. Preparation of fermented or germinated foods or addition of cultures of Lactobacillus *plantarum*, Lactobacillus*fermentum*, and Lactobacillus acidophilus as starter culture duringfermentation improve nutrient bioavailability and starch functionality (Kaur *et al.*, 2023). Moreover, consumption of millet prebiotics stimulates the immune system and reduces hypercholesterolemia. Moreover, studies have shown the anti- glycaemic response of millet-based food (Bunkar *et al.*, 2021) which makes millets a functional food in the management of type-2 diabetes Moreover, studies have also shown the effect of millet consumption against cardiovascular diseases, colon cancer, and celiac disease (Bhat *et al.*, 2018). Interestingly millet polyphenols exert a positive effect on resistant starch of millets which enhances the inhibitory effect of millets against metabolic enzymes like amylases and glucosidases and health promoting effect of millet resistant starch (Annor *et al.*, 2017). Additionally, the synergistic effect of millet nutritional constituents like starch digestibility have been elucidated. The interaction of millet starch with protein, lipid, and polyphenols through complexing affect millet starch digestibility by reducing its gelatinization and permeability towards digestive enzymes (Zheng*et al.*, 2020).In another study effect 30% and 48% supplementation of foxtail millet affected glucose metabolism and gut microbiota in rats. The supplementation significantly decreased blood glucose and triglycerides and improved blood glucose tolerance, insulin resistance, & abundance of probiotic bacteria and butyrateswith a dose dependent relationship (Ren *et al.*, 2022). Wang *et al.* (2023) investigated the effect of heat-treated foxtail millet starch and protein on type 2 diabetic mice and its influence on gut microbiome and metabolic profile. The consumption of heat-treated foxtail millet starch reduced fasting blood glucose (18.52%) and insulin levels (15.96%). In addition, heat-treated foxtail millet starch altered the gut microbiota composition, enriched the abundance of probiotics and short-chain fatty acids producing bacteria, reduced harmful bacteria, and increased fecal short-chain fatty acids concentration. A preventive effect of modified bran from finger millet and kodo millet was observed against high fat induced obesity, liver dyslipidemia, oxidative stress, inflammation, visceral white adipose tissue hypertrophy, and lipolysis in mice (Devi *et al.*, 2023).

5. Millet starches – application

Millet starch is used either in its native or modified forms in the food and non-food industry. Generally, native and modified starches are used as a binder, thickeners in baked food items, meat products, snack seasonings, as a fat replacer in ice creams, flavor encapsulating agents, emulsion stabilizers in juices, beverages, gelling agents in gums, and gels, foam stabilizer in marshmallows, and as crisping agent for the fried snack products, drug deliver as nano particles, edible films (Sandhu *et al*., 2019). The pearl millet native and chemically modified starch has been reportedly used as fat replacer and to reduce syneresis in white sauce (Sharma *et al*., 2017). Furthermore, the modification of millets starches reduces its gelatinization temperature, improves its solubility, paste viscosity, clarity, and water binding capacity which presents them as an appropriate thickening and stabilizing ingredient in gravies, sauces, and ketchups. Modified starches are also used as texture enhancers in ice creams. The starches reduce the viscosity of aqueous phase of ice-cream thus, reducing the formation of ice crystals. The chemically modified pearl millet starch has been found as an effective fat replacer in cold desserts as compared to other replacers like whey protein concentrate, inulin, and corn starch (Sharma *et al*., 2018) in terms of sensory and thawing characteristics. Millet starches which are chemically modified presents a superior material for the development of edible coatings or films. Millet starch based edible films exhibit improved flexibility, transparency, and reduced water vapour permeability. Moreover, blending of millet starches with gums further enhances the film properties which can be utilised for packaging and coating application (Ju & Song, 2019).A study investigated the modified pearl millet starch for preparation of white sauce. The pearl millet starch was modified by addition of propylene oxide. Syneresis was nor observed in white sauces containing hydroxypropylated pearl milletstarches after 14 days of storage. The sensorial analysis of modified pearl millet starch obtained maximum acceptance in terms of consistency, graininess, taste, and overall acceptability (Shaikh *et al*., 2020).

The emerging demand of fiber rich gluten free products among consumers also bringing attention towards the use of millet resistant starch in food products in place of dietary fibers. The higher incorporation of dietary fiber in order to enhance the nutritional content of food product compromises with its sensorial and texture acceptability. Millets RS are significant replacement of wheat for development pf gluten free bakery products like breads, biscuits, cookies, pancakes, and waffles (Onyango*et al*., 2020).

Conclusion

Millets are grown in the arid and semi-arid regions and their better adaptability to environmental stress conditions makes them a superior choice for sustainable cropping system. Millets offers various health promoting and therapeutic advantages. Due to cost effective nature of millet cropping they ensure potential supply of starch at low prices. Starch is a major component of milletgrains,but it is neglected for its utilization as raw material to producecommercial grade starch. The native starch is extracted from millets, however, due to low solubility, poor sheer stability, and high degree of retrogradation native starches are modified by various methods. The modified starch has significant changes in the structural and digestibility characteristics. The native and modified millets starches have potential scope of utilisation in food and non-food applications like development of edible coatings and pharmaceutical industry. Furthermore, the challenges and limitations in millet processing can be addressed to enhance promising utilization of millet starch for industrial applications.

Declaration of Competing Interest

The authors declare that they have no known competing interests.

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