Plant Archives Vol. 15 No. 1, 2015 pp. 15-21 ***ISSN 0972-5210***

EFFECT OF HEAT MOISTURE TREATMENT ON FUNCTIONAL AND PHYTOCHEMICAL PROPERTIES OF NATIVE AND MODIFIED MILLET FLOURS

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Abstract

Millets are one of the oldest foods known to humans and cultivated since time immemorial. Millets are termed as nutricereals since, they are nutritionally superior to major cereals with respect to protein, energy, vitamins and minerals. The functional properties and phytochemical components of native and modified millet flours were studied. The functional characteristics such as water absorption index (WAI) and water solubility index (WSI) were maximum in native flour than modified millet four. The data projected for water absorption capacity (WAC) and oil absorption capacity (OAC) of modified millet flour was high when compared with native flour. The soluble, insoluble and total dietary fibre content was observed to be high in modified millet flour than native flour. Among the native flours, little millet contained higher proportions of polyphenols (373.67 ± 12.16 mg GAE/100 g), antioxidant activity was 83.27 ± 2.28 mg AAEAA/100g in pearl millet, phytate content was 35.17 ± 0.63 mg/100g in kodo millet (35.17 ± 0.63 mg/100g) and tannin content was 22.67 ± 0.21 mg TAE/100g, respectively in proso millet flour followed by other millet flour.

Key words : Native flour, modified millet flour, functional characteristics, dietary fibre, phytochemical components.

Introduction

Current dietary guidelines focus on lowering dietary fat and increasing complex carbohydrate intake, such as starch and dietary fiber. The dietary fibre and resistant starch of minor millets have been attributed to exhibit hypoglycemic and hypolipidemic effects (Pathak and Srivastava, 1998). Dietary fibers are important for their hypoglycemic effect, hypolipidemic effect; lowering serum cholesterol hence helps in prevention of atherosclerosis, antitoxic effect and anti-cancerous effect. Glycemic index could be attributed to development of resistant starch during heating and cooling cycles. Heating and cooling cycles significantly increased resistant starch fraction in millets. Resistant starch (defined as any starch that escapes digestion in small intestine) was reported to exhibit a wide range of health benefits such as lowering caloric density and low glycemic response. It was also reported to lower digestibility and act as a fecal bulking agent. Resistant starch, an important starch derivative could be obtained by modification of starches. Starch is classified into rapidly digestible starch (RDS), slowly digestible starch (SDS) and resistant starch (RS) according to the rate of glucose release and its absorption in the gastrointestinal tract. RDS is the starch fraction that causes a sudden increase in blood glucose level after ingestion and SDS is a starch fraction that is digested completely in the small intestine at a lower rate as compared to RDS. RS is the starch portion that cannot be digested in the small intestine, but is fermented in the large intestine. The health benefits of RS have been reported as prevention of colon cancer, hypoglycemic effects, substrate for growth of the probiotic microorganisms, reduction of gall stone formation, hypocholesterolemic effects, inhibition of fat accumulation, and increased absorption of minerals. The potential health benefits of SDS are linked to a stable glucose metabolism, diabetes management, mental performance and satiety. Slowly digestible starch content was increased by autoclaving cooling cycle method. Slowly digestible starch, an important starch derivative could be obtained by modification of starches.

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Starch modification is a process of altering the starch structure by affecting the hydrogen bond in a controllable manner. Heat moisture treatment (HMT) is one of many physical methods used to modify starch. HMT is a hydrothermal modification method that has commonly been explored to alter the physicochemical, digestibility, and functional properties of starch with minimum effect on the granule structure (Jacobs and Delcour, 1998). Acid modification of starch is a granular modification of the native starch achieved through treatment of starch below its gel point in aqueous acid suspension (Wang and Wang, 2001). An enzymatic modification involves the exposure of starch suspensions to a number of enzymes primarily, including hydrolyzing enzymes that tend to produce highly functional derivatives. The aim of the present study is to modification of starch from the millet by physical modifications and investigating the behavior of the native and modified starches.

Millets contain good sources of dietary fiber, minerals and phytochemicals with antioxidant activity. Phytochemicals (phenolic compounds and phytates) are responsible for higher antioxidant activity in whole grain foods (Sridevi *et al*., 2008). Millet has been shown to be helpful in type 2 diabetes mellitus, cardiovascular disease and cancer due to its low glycemic index and antioxidant activity (Hathan and Prasanna, 2011). The hypoglycemic effect of millets with their high crude fiber, dietary fibre, antioxidant, low carbohydrate content, low digestibility and also have β-glucans, which are water soluble gums helpful in impairing glucose metabolism (Itagi *et al*., 2012).

Minor millets like kodo are also described as nutritious millet and have received far less research and development attention than other crops with regard to crop improvement and utilization. It is the main source of protein and minerals in the daily diets of tribal and weaker section living in remote rural areas. Millets including kodo contain water soluble fiber and this property may be utilized for maintaining or lowering blood glucose response among diabetic and CVD patients. Little millet is rich in fibre content when compared to other small millets. Little millet has a significant role in providing nutraceutical components such as phenols, tannins and phytates along with macro and micro-nutrients. Pearl millet is the most widely grown type of millet. Nutritionally, pearl millet is superior to major cereals with reference to energy value, high quality proteins, fat and minerals such as calcium, iron, zinc. Besides, it is also a rich source of dietary fiber and micro nutrients (Anusehgal and Kwatra, 2006; Malik *et al*., 2002).

Materials and Methods

Whole wheat (*Triticum aestivum*), kodo millet (CO 3) (*Paspalum scrobiculatum*), little millet (CO 6) (*Panicum sumatrens*), pearl millet (COC 9) (*Pennisetum typhoideum*) and proso millet (COPV 5) (*Panicum miliaceum*) were collected from Department of Millets, Centre for Plant Breeding and Genetics, Tamil Nadu Agricultural University, Coimbatore (Tamil Nadu), India.

Preparation of sample

Optimization technology for the development of modified flour from millets

To optimize the technology for the development of modified flour to utilize as the functional food ingredient, the physical modification method has been followed.

Physical modification (Autoclaving-Cooling Cycle)

The physical modification (autoclaving - cooling cycle method) technique was used and followed as per the standard Berry (1986) procedure for the preparation of modified starch (kodo millet, little millet, pearl millet and proso millet) with slight modification. The kodo millet and pearl millet grains were cleaned, washed separately and soaked for 2 hours, ground and then it was pressure-cooked at 121° C (15 lb/in^2) for one hour in an autoclave. The gelatinized starch mixture was cooled to room temperature and it was frozen at 4^{o}C for 24 hours, which was termed as one cycle. Then, three additional cycles were carried out, followed by cabinet-drying for about 4-6 hours at 40^{o}C according to the respective starches and ground into fine particles and packed in air-tight container.

Functional properties of native and modified millet flours

Water absorption index and water solubility index

Water absorption index (WAI) and water solubility index (WSI) were studied by the method described by Anderson *et al*. (1969). Water absorption capacity (WAC) of flours was measured by the centrifugation method described by Sosulski and Garratt (1976). Oil absorption capacity (OAC) of flour was measured by the centrifugation method described by Lin and Humbert (1974).

Colour value

Colour value of flour was measured by using Hunter Lab Colorimeter. Hunter lab calorimeter value L*(0=black, 100=white), a* (+value = red, -value = green) and b*(+value = yellow, -value = blue) values were recorded (Hathorn *et al*., 2008).

Phytochemical components of dietary fibre

The soluble, insoluble and dietary fiber was quantified by Hellendoorn technique (James and Theander, 1981).

Phytochemical components

Total phenols, tannin and phytate contents were determined by the spectrophotometric method of Sadasivam and Manicam (2008). The radical scavenging ability of the sample was tested on the basis of the radical scavenging effect on the DPPH free radical by Goupy *et al*. (1999).

Statistical analysis

The experiments were conducted in triplicates and the data were expressed as mean± standard deviation (S.D).

Results and Discussion

Functional properties of native and modified millet flours

Water absorption index (WAI), water solubility index (WSI), water absorption capacity (WAC) and oil absorption capacity (OAC) of native flour and modified millet flour were presented in table 1.

Water Absorption Index (WAI)

The water absorption index measures the volume occupied by the starch after swelling in excess water, which maintains the integrity of starch in aqueous dispersion. Results showed that the highest WAI was observed in wheat flour (9.10 ± 0.42 g/100g). The WAI was maximum in native flour ranged from 7.40 ± 0.32 to 8.72 ± 0.15 g/100g than modified millet four ranged from 5.24 ± 0.22 to 5.69 ± 0.13 g/100g respectively. Adebowale *et al*. (2005), similarly reported that the annealing of cassava starch and heat moisture treatment and annealing of red sorghum starch (modification), respectively decreased starch swelling power and increased swelling power as the temperature increased. Similar trend was noted in the present investigation also.

Water Solubility Index (WSI)

The water solubility index of wheat flour was 3.40 ± 0.07 g/100g. Water solubility index as related to the presence of soluble molecule, for the native flour which ranged between 6.16 ± 0.13 and 9.62 ± 0.35 g/100g and the WSI of modified millet flour ranged between 1.32 ± 0.02 and 4.04 ± 0.15 g/100g, respectively. The swelling power and solubility of starch granules showed a great evidence of interaction on the starch chains between the amorphous and crystalline regions. When starch was subjected to heating in excess water, there is a relaxation of the crystalline structure and the groups of amylose and amylopectin associate with water molecules through hydrogen bonding. This causes an increase in the swelling power and the solubility of the granules (Hoover, 2001). Several researchers have reported that structural disruption within the starch granules, after autoclave-cooling treatment might be responsible for the reduction in swelling capacity and starch solubility (Leach *et al*., 1959). According to Saguilan *et al*. (2005) autoclaved samples presented lower solubility than corresponding native starches. This pattern agrees with the higher RS content recorded for the autoclaved samples, which produced higher amount of insoluble material (decreased solubility values) and also results in a low water retention feature (swelling power). These findings also support the present investigation.

Water Absorption Capacity (WAC)

The data projected for water absorption capacity of modified millet flour was high when compared with native flour. The WAC was maximum in wheat flour (78.80 ± 3.26 ml/100g). The WAC of native flour ranged between 74.08 ± 1.78 and 76.83 ± 3.38 ml/100g. When modification the WAC was observed to be high and it was ranged between 82.07 ± 3.45 and 88.43 ± 3.33 ml/100g, respectively. Water binding capacity of modified starch was highest due to high amylose content of RS3. It is known that amylose has higher water binding capacity than native starch (Zhiqiang *et al*., 1999).

Oil Absorption Capacity (WAC)

The oil absorption capacity was found to be maximum in modified millet flour than native flour. The OAC of wheat flour was 87.27 ± 3.87 ml/100g. in the native flour, the maximum OAC was recorded to be 85.57 ± 3.00 ml in pearl millet flour followed by little millet flour (84.36 ± 3.27 ml), kodo millet flour (74.74 ± 3.00 ml/100g) and proso millet flour (73.58 ± 2.18). Modified millet flour had the highest OAC and the value was 87.45 ±3.54 in kodo millet flour followed by little millet flour (86.91 ± 2.13ml/100g), proso millet flour (86.64 ± 2.24) and pearl millet flour (85.82 ± 2.32 ml/100g), respectively. Helen (2010) found that the processed (germination and fermentation) finger millet flour also had a higher oil absorption capacity in the range of 74.43-126.38, which was significantly higher than that of controlled flour (71.40). Abulude *et al*. (2005) also stated that water and oil absorption of finger millet flour increased during germination.

Colour index of native and modified millet flours

Table 2 presents the results of the colour index of native and modified millet flour and pulse flour. The varietal differences were observed for various Hunter colour parameters. The colour of starch affects the colour of the finished product. A bright white colour starch is

Table 1 : Functional characteristics of native and modified millet flours.

Millets	Water absorption index (g/100 g)		Water solubility index (g/100 g)		Water absorption capacity (ml/100g)		Oil absorption capacity (ml/100g)	
	Native flour	Modified flour	Native flour	Modified flour	Native flour	Modified flour	Native flour	Modified flour
Kodo millet	8.27±0.31	5.39±0.18	9.08±0.28	4.04±0.15	74.93±2.86	82.07±3.45	74.74±3.00	87.45±3.54
Little millet	8.72±0.15	5.69±0.13	6.68±0.21	1.32±0.02	76.83±3.38	88.43±3.33	84.36±3.27	86.91±2.13
Pearl millet	8.25±0.30	5.24±0.22	9.62±0.35	2.76 ±0.01	74.08±1.78	83.53±2.54	85.57±3.00	85.82±2.32
Proso millet	7.40±0.32	5.26±0.11	6.16±0.13	1.72 ±0.06	75.30±3.25	87.77±3.78	73.58±2.18	86.64±2.24

All data are the Mean ± SD of three replicates.

Table 2 : Colour value of native and modified millet flours.

Millets		Colour		
		L*	a*	b*
Kodo millet	Native flour	117.75±3.03	-6.25±0.05	12.40±0.47
	Modified flour	133.21±2.43	-6.55±0.06	17.50±0.42
Little millet	Native flour	121.23±2.79	-6.29±0.04	11.13±0.48
	Modified flour	130.87±4.24	-6.52±0.21	16.96±0.47
Pearl millet	Native flour	103.94±4.40	-3.26 ±0.04	37.97±1.54
	Modified flour	111.94±2.02	-3.66±0.07	47.02±1.06
Proso millet	Native flour	126.62±1.70	-6.67±0.07	31.10±1.33
	Modified flour	137.40±1.98	-7.66±0.07	31.22±1.00

Results are Mean ± SD of three determinations.

Table 3 : Phytochemical components of native and modified millet flours (mg/100g).

Millet flours	Total polyphenols (mg/100g)		Antioxidant (mg AAEAA/100g)		Phytate (mg/100g)		Tannin (mg TAE/100g)	
	Native flour	Modified flour	Native flour	Modified flour	Native flour	Modified flour	Native flour	Modified flour
Kodo millet flour	368.77±11.17	362.38±14.08	70.82±3.07	66.85±2.55	35.17± 0.63	34.67±0.31	22.53±0.24	20.57±0.73
Little millet flour	373.67±12.16	369.84±11.33	67.63±1.22	63.92±1.21	24.42±0.55	23.87±0.26	18.62±0.15	16.67±0.31
Pearl millet flour	333.63±13.23	328.68±13.36	83.27±2.28	80.73±2.41	33.42±0.52	32.92±0.31	13.45±0.39	12.78±0.54
Proso millet flour	361.87±10.54	357.85±14.52	65.74±2.07	61.85±1.84	27.17±0.47	26.32±0.97	22.67±0.21	20.64±0.87

Results are Mean ± SD of three determinations.

more desirable for product development. The L* value was a parameter for characterizing starch colour, its lightness and it was a direct measurement of its whiteness. The L* value close to 100 indicates whiteness. The chromaticity coordinate a*, which ranges from -60 (green) to +60(red), the chromaticity coordinate b*, which ranges from -60 (blue) to +60 (yellow), indicated a higher intensity of yellow.

Colour changes gives information about the extent of browning reactions such as caramalization, maillard reaction, degree of cooking and pigment degradation that take place during the starch extraction process (Altan *et al*., 2008).

The modification of millet flour showed the highest values for the luminosity parameter L* value, Chroma a* values and b* values than native flour. The colour of L*, a* and b* value was 129.53 ± 5.49, 5.52 ± 0.01 and 29.48 ± 0.89 in wheat flour. The colour of L* was , a* and b* value of modified millet flour ranged between 111.94 ± 2.02 and 137.40 ± 1.98, -3.66 ± 0.07 and -7.66 ±

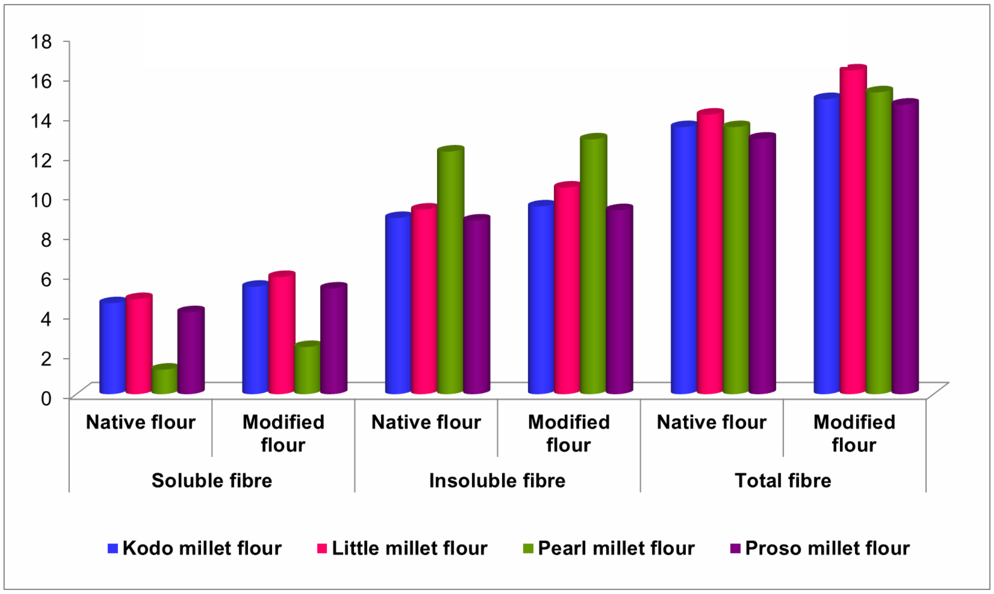

Fig. 1 : Dietary fibre (g/100g) profile of native and modified millet flours.

0.07 and 17.50 ± 0.42 and 47.02 ± 1.06, respectively. The colour value of hydrothermally processed millet was darker than native millet and decorticated millet (Shobana, 2009). Helen (2010) found that the time of fermentation increased the color of flour also increased, while vice versa during germination process. However, during cooking the color of germinated flour was darker than the other treatments (Kikafunda *et al*., 2006).

Dietary fibre profile of native and modified millet flours

The data pertaining to dietary fibre profile of native flour and modified millet flour are presented in fig. 1. The soluble, insoluble and total dietary fibre content was observed to be high in modified millet flour than native flour. Native flour, the soluble fibre content was observed to be high in little millet flour (4.78 ± 0.01) followed by kodo millet flour (4.57 ± 0.05), proso millet (4.12 ± 0.03), wheat flour (1.63 ± 0.02) and pearl millet flour (1.23 ± 0.02), insoluble fibre content ranged from 5.69 ± 0.23 to 12.20 ± 0.47 and total dietary fibre content ranged between 7.32 ± 0.33 and 14.06 ± 0.36 g/100g. Modified millet flour, the soluble fibre content was 5.89 ± 0.05, 5.40 ± 0.02, 5.31± 0.05 and 2.37 ± 0.05 g/100g in little millet flour, kodo millet flour, proso millet flour and pearl millet flour. The insoluble and total dietary fibre content ranged from 9.44 ± 0.36 to 12.81 ± 0.55 and 14.84 ± 0.41 to 16.28 ± 0.50 g/100g respectively. Millet contain appreciable amount of dietary fibre (9-16%) even after removal of husk and major portion of bran (Hadimani and Malleshi, 1993). Roopa *et al*. (2012) found that soluble dietary fibre content of little millet contained 3.01 to 3.25 g/100 g, insoluble dietary fibre was 5.15 to 5.24 g/100 g and total dietary fibre content was 8.25 to 8.60 g/100 g respectively. Florence and Asna (2011) found that the insoluble dietary fibre content of pearl millet ranged from 10.9 to 12.6 g/100g, soluble dietary fibre (0.70 to 1.05), total dietary fibre (11.9 to 13.3 g/100g).

Phytochemical components of native and modified millet flours

Phytochemical components of native and modified millet flours are given in table 3. Phytochemical components such as total polyphenols, antioxidant activity, phytate and tannin were observed to be high in native flour than modified millet flour by heat moisture treatment or autoclaving and cooling cycle method. There will be reduction in phytochemical components due to heat moisture treatment of millet and this may provide nutritional advantages with respect to increased bio-availability of minerals and protein. Modification of millets improved its nutritive value by decreasing the tannin content, improving *in vitro* protein digestibility and *in vitro* starch digestibility.

Among the native millet flours, little millet flour contained higher proportions of polyphenols (373.67 ± 12.16 mg GAE/100 g) than kodo, proso and pearl millet flour (368.77 ± 11.17, 361.87 ± 10.54 and 333.63 ± 13.23 mg GAE/100g). Similar study by Chethan and Malleshi (2007) revealed that finger millet brown varieties contained (120-230 mg/100g) higher proportions of polyphenols than white (30 - 50 mg/100g) varieties. The polyphenol content of the millet varieties ranged from 30 to 230 mg/100g. The tiny millet grain has a dark brown seed coat, richer in polyphenols compared to other continental cereals such as barley, rice, maize and wheat (Viswanathan *et al*., 2009). Hotz and Gibson (2007) also stated that certain tannins and other polyphenols in legumes and sorghum may also be reduced during germination as a result of formation of polyphenols complexes with proteins and the gradual degradation of oligosaccharides. Such reductions in polyphenols may facilitate iron absorption. An inverse relationship between tannin content and *in vitro* protein digestibility has been reported for germinated finger millet (Mbithi *et al*., 2000). Elyas *et al*. (2002) stated that natural fermentation of pearl millet decrease polyphenols and phytic acid and causes no changes in tannin contents.

Antioxidant activity was high in pearl millet flour (83.27 ± 2.28 mg AAEAA/100g) followed by kodo millet, little millet and proso millet (70.82 ± 3.07, 67.63 ± 1.22 and 65.74 ± 2.07 mg AAEAA/100g, respectively). Similar study by Ismail *et al.* (2010) examined total antioxidant capacity of finger, little, foxtail and proso millets were found to be higher. The phytate content was maximum in kodo millet flour (35.17 ± 0.63 mg/100g) whereas pearl millet, proso millet and little millet contained 33.42 ± 0.52, 27.17 ± 0.47 and 24.42 ± 0.55 mg/100g, respectively. The tannin content was maximum in proso millet flour (22.67 ± 0.21 mg TAE/100g, respectively) followed by kodo millet, little millet and pearl millet (22.53 ± 0.24, 18.62 ± 0.15 and 13.45 ± 0.39 mg TAE/100g, respectively).

Conclusion

The functional properties and phytochemical components of native and modified millet flours were studied. Results obtained in this study indicated that the millets are a good source of soluble, insoluble and total fibre content. Phenolic compounds and antioxidant activity was high in almost all millets.

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