

Physico- chemical changes in milk constituents during manufacture and storage of Khoa and Paneer

India is emerging as the highest milk producing country in World with an annual production of 140 million tonnes. A large quantity of milk produced in the country amounting to over 54% is being converted into various milk products; share of the traditional milk products comes to about 37%. The market value of traditional products is considered to about to be 578 billion. The consumption of traditional milk products is likely to grow at an annual growth rate of more than 20%.

Traditional dairy products play a significant role in the economic, social, religious and nutritional wellbeing of the Indian masses .It is still mostly prepared, packed and or marketed by old traditional method without mechanization or well documented standardization of the process under unsanitary condition and have a poor shelf life. However, these products offer several technological benefits, viz. their mass appeal, lower cost of production, simple manufacturing technique, adopted at rural level/ collection centre, high profit margin, generate lots of employment , value added products and nutritional status and have high export potential . The classification of these products based on the principle of their manufacture is given below.

Classification of Traditional Dairy Products

Type	Base Material	End Products
Acid coagulated	Chhana Paneer	rosogolla,sandash,pantoa,cham-cham,chhana mukri,chhana-podo,sitabhog Culinary dishes
Heat desiccated	Khoa -	Peda,burfi,kalakand, milk cake ,gulabjamun,rabri
Fermented/cultured	- Chakka	Dahi.,misti doi,lassi Shrikhand,shrikhand wadi
Fat rich	Ghee	Fat rich
Frozen	-	Kulfi/malai
Cereal based	-	Kheer,payasam,firni

Paneer:

Paneer is an indigenous white (soft) cheese (unripened) which is used extensively as an ingredient in many vegetable delicacies. About 4 -5 % of the total milk produced in India is converted into paneer .Good quality paneer is obtained when standardised buffalo milk (fat:SNF, 1:1.65) heated to 90°C and coagulating the milk with 1% citric acid at 70°C and also characterized by a white colour, sweetish, mildly acidic, nutty flavour, spongy body and close knit texture.

Definition of Paneer:

According to Prevention of FSSA (2006), paneer is the product obtained from cow or buffalo milk or combination thereof by precipitation with sour milk, lactic acid or citric acid. Milk solids may be used in preparation of this product. It shall not contain more than 70% moisture and the milk fat content shall not be less than 50% of the dry matter. Paneer when sold as low fat chhana, it shall not more than 70% moisture and the milk fat content shall not more than 15% of dry matter.

Coagulants used: Lactic acid, Citric acid, Malic acid, Vinegar, Glucono delta lactone, Sour whey.

Chemical composition of paneer

Parameter (%)	Cow	Buffalo
Moisture	52 – 54	50 – 52
Fat	24 – 26	28 – 30
Protein	16 – 19	13 – 15
Lactose	2.0 – 2.2	2.2 – 2.4
Ash	2.0 – 2.3	1.9 – 2.1

Specification of *paneer* according to FSSR (2011)

Parameter	<i>Paneer</i>	Low fat <i>Paneer</i>
Moisture, maximum, %, (m/m)	60.0	60.0
Milk fat, %, (m/m), dry matter basis	50.0 (minimum)	15.0 (maximum)

Milk (preferably buffalo milk) is heated to about 90°C and coagulated at 70°C using mostly citric acid as coagulant. Whey is then drained through cloth lined hoops and pressing the coagulated to form blocks. Blocks thus formed are floated in chilled water for firming heir body. The cow and buffalo milk mixed

in the ratio of 50:50 having a fat content of 5% yields a superior product than cow milk alone.

Factors influencing the quality of Paneer:

1. **Quality of milk:** Acidic milk having a titratable acidity of 0.2 to 0.23% LA yields a product with inferior quality. Homogenisation of cow milk is recommended to bring about improvement in the yield and to improve the organoleptic score of paneer.
2. **Heat Treatment of milk:** Heating milk to 80°C for 5 min and cooling to 70°C before coagulation affects the sensory and microbiological quality of paneer.
3. **Type of coagulant:** Different coagulant like citric acid solution, one day old whey, 48 hr old sour whey, whey cultured with *L. acidophilus* have been used to prepare paneer. In addition to this coagulant such as hydrochloric acid, phosphoric acid, tartaric acid and acetic acid have also been used in the manufacture of paneer.
4. **Strength of coagulant:** Best quality paneer can be obtained using 1 % citric acid. Two percent citric acid also yielded good quality paneer when cow milk is used. Satisfactory quality products are obtained when non-conventional coagulants like hydrochloric acid and *acidophilus* whey (0.6%) are used.
5. **Amount of coagulant:** For making good quality paneer from cow milk 2.34g citric acid or lactic acid is required for 1kg of milk while for buffalo milk 2.1 g of citric acid or lactic acid per gram is required.
6. **Coagulation Temperature:** Coagulation temperature of 70°C has been suggested to be most effective. However good quality paneer can also be prepared at a coagulation of 80°C from both the milk.
7. **pH of coagulation:** The optimum pH of coagulation is 5.35 for buffalo milk and 5.0 for cow milk.

The yield of paneer decreases with increase in the strength of coagulant, coagulation temperature and lowering the pH of coagulation in case of buffalo milk and it increases with increase in the coagulation temperature in cow milk paneer. The yield of paneer can also be increased by co-precipitation of casein and whey protein. Higher level of fat in paneer milk leads to lower yield of the product in case of buffalo and cow milk. Homogenisation of paneer milk improved the paneer yield.

Chemistry of coagulation process in paneer:

The phenomena involves the formation of large structural aggregates of casein from the normal colloidal dispersion of discrete casein micelles, in which milk fat and coagulated serum proteins are entrapped together with whey. The major changes that takes place during coagulation are

1. The progressive removal of tri calcium phosphate from the surface of casein and its conversion into mono calcium phosphate and soluble calcium salt.
2. Progressive removal of calcium from calcium hydrogen caseinate to form soluble calcium salt and free casein
3. When the pH of milk system drops, the colloidal particles become isoelectric, i.e. the net electric charge becomes zero. Under such circumstances the dispersion is no longer stable; the casein gets precipitated and forms a coagulum.

The development of typical rheological characteristics of paneer could be due to preponderant and intensive heat induced protein – protein interaction. It is believed that β lactoglobulin and K- casein interact by sulphhydryl disulphide inter change when heated together. It is initiated at 65°C, increases up to 83% at 85°C and then decreases to 76% at 99°C.

KHOA

Khoa is a heat desiccated milk product. About 7-8% of the total milk produced in India is converted into khoa. It is prepared traditionally by desiccating milk in an open shallow pan with continuous stirring till a coagulation mass is obtained which is worked up to form a pat. It is used as a base material for a large number of milk sweets such as burfi, peda, milk cake, kalakand, gulabjamun, etc. Three distinct types of khoa, namely, pindi, dhap and danadar are available

in the country. These varieties differ in quality, texture, composition and specific usage. Khoa generally contains 17-20% protein, 22-25% lactose and 100-130 ppm of iron depending on whether it is prepared from cow, buffalo or mixed milk.

Specification of Khoa according to FSSR, (2011):

Parameters	Khoa
Total solids, minimum, %, (m/m)	55.0
Milk fat, minimum, %, (m/m), dry matter basis	30.0
Total ash, maximum, %, (m/m)	6.0
Titratable acidity (as % lactic acid), maximum, %	0.9

Definition of Khoa:

According to FSSA (2006), khoa by whatever variety of names it is sold such as pindi, danedar, dhap, mawa or kava means the product obtained from cow or buffalo or goat or sheep milk (or milk solid) or a combination thereof by rapid drying . The milk fat content shall not be less than 30 % on dry matter basis of the finished product. It may contain citric acid not more than 0.1% percent by weight. It shall be free from added starch, added sugar and added colouring matter.

Buffalo milk is usually preferred over cow milk for khoa making, since the former gives higher yield and has a more desirable flavour, body and texture.

Different type of Khoa:

1. Pindi

It is characterized as a circular ball of hemispherical pat with smooth and homogeneous body and texture. This poses characteristic cooked flavour and is preferred for the preparation of burfi and peda. It contains 19% moisture; 37% fat; 18% protein; 22% lactose and 3.6% ash.

2. Danedar

Granular texture and uneven body characterize this form of khoa. Usually 0.1% of citric acid (on product basis) is added during the heat desiccation process in shallow pan to obtain such texture. It has 20-25% fat and 35-40 % moisture. This forms base for the preparation of kalakand (granular texture), milk cake and granular milk solids.

3. Dhap:

It is characterized by loose and sticky body and smooth texture, attributable to higher moisture content and less intensive heat treatment. It contains about 20-23% fat and 37-44% moisture. It is preferred for the preparation of gulabjamun.



Dhap Khoa



Danedar Khoa



Pindi Khoa

Chemistry of Khoa

Khoa is essentially a matrix of heat denatured milk protein, in which fat, lactose; minor constituents and moisture are entrapped. Protein-protein reaction and reaction with other milk constituents occur during desiccation. Lactose and protein that undergo Maillard browning and caramelization are significant in imparting typical flavour and desirable sensory characteristics to the khoa.

The main reaction in the preparation of khoa is the heat denaturation and coagulation of milk protein particularly the serum proteins and their interaction with casein and other constituents. Most of the albumin and globulins are almost denatured; the protective properties of the other colloids are destroyed early in the boiling process. Casein is also irreversibly denatured from colloidal state to non-dispersible state. The denaturation is accelerated by the incorporation of air and frothing during stirring. Total heat coagulation of protein occurs when the boiling mixture thickens to a buttery consistency in the pan.

Fat globules in milk, undergo subdivision and disrupts the fat globule membrane as a result of heat, vigorous agitation and scraping during the manufacture of khoa. Almost half of the globular fat is released as free fat, the extents of which depend upon the type and amount of fat content in the milk.

Formation of free fat during transition from liquid phase to the semi-solid phase is very significant for the development of typical flavour, body and texture of khoa. The short chain fatty acids decreases, medium chain fatty acids increases and long chain fatty acids are unaffected during the preparation of khoa. The lactose is present in khoa mostly as supersaturated solution. Generally lactose does not crystallize out due to high viscosity and coagulations of proteins. However, large crystals of lactose are found in ordinary khoa.

A portion of milk salt is precipitated during preparation of khoa. Iron content, probably derived from heating pan, is raised considerably. Vitamin A, thiamine, riboflavin, ascorbic acid, nicotinic acid and folic acid are decreasing in the course of heating of milk for making khoa.

The deterioration of khoa is attributed to unhygienic methods of processing and subsequent improper handling, followed by lactose breakdown, proteolysis and lipolysis due to activities of the mixed flora during storage. Being aerobic in nature, moulds cover the entire surface of the product kept under ambient conditions producing an abnormal colour, flavour and appearance.

Changes occurred during manufacture of Khoa:

1. Change in state
2. Change in intensity of colour
3. Change in milk fat
4. Heat coagulation of milk protein
5. Change in lactose
6. Precipitation of milk salts
7. Increase in iron content
8. Changes in vitamins

Chemical changes of khoa during storage:

Khoa has a low keeping quality at room temperature and develops rancid flavour. This may be due to fat hydrolysis which is due to lipase action. Mouldy surface developed during storage are due to high moisture content and excessively high humidity of storage room. When stored at low temperature (5 – 10°C) for long time staleness developed. There is an increase of various types of microorganism during storage at room temperature. The shelf life of khoa is about 2-4 days under ambient condition and 3 weeks under refrigerated conditions.

Chhana

Chhana is a heat-acid coagulated milk product obtained by acid coagulation of boiled hot whole milk and subsequent drainage of whey. It is creamish-white in appearance with compact spongy body, sweetish-acidic flavour.

According to FSSAI (2006), chhana is the product obtained from cow or buffalo milk or combination thereof by precipitation with sour milk, lactic acid or citric acid. Milk solids may be used in preparation of this product. It shall not contain more than 70% moisture and the milk fat content shall not be less than 50% of the dry matter. Chhana when sold as low fat chhana, it shall not contain more than 70% moisture and the milk fat content shall not more than 15% of dry matter.

Chemical Composition of Chhana (FSSAI, 2011):

Parameter	<i>Chhana</i>	<i>Low fat Chhana</i>
Moisture, maximum, %, (m/m)	65.0 (for <i>Chhana</i>)	65.0 (for <i>Chhana</i>)
Milk fat, %, (m/m), dry matter basis	50.0 (minimum)	15.0 (maximum)

Chemistry of chhana processing:

The process of coagulation of milk in the preparation of chhana due to combined chemical and physical changes in casein brought about by the action of acid and high temperature of coagulation. This involves the formation of large structural aggregates of casein or curd from the normal colloidal dispersion of discrete casein micelles in which fat and coagulated serum protein are entrained together with whey. Then the curd separates from the milk serum as a flocculent. A part of calcium and phosphate losses from the casein micelles during boiling and subsequent coagulation.

Various factors influencing the quality of chhana:

1. Type of milk
2. Fat content in milk
3. Homogenization

4. Calcium level
5. Additives
6. Type and amount of coagulant
7. Temperature of coagulation
8. pH of milk
9. Speed of stirring

Type of milk:

Cow milk is preferred for chhana preparation since it yields a **soft body, smooth texture and small grain** that are suited for making sweet. The chhana from buffalo milk has a slight hard body, a greasy and coarse texture. Buffalo milk contain higher concentration of casein, mainly in the miceller form with bigger size of the micelles, higher proportion of high melting triglycerides and higher content of calcium may be responsible of hard body and coarse texture in buffalo milk chhana.

Fat content in milk:

Fat level in milk affect the final quality of chhana. A minimum fat level of 4% in cow milk and 5% in buffalo milk is essential for satisfactory quality of chhana. Higher fat level would give rise to a softer chhana with higher fat loss in the whey.

Presence of colostrum:

The presence of colostrum in milk tends to produce a pasty texture in the coagulation mass. The adulteration of milk with starch results in a gelatinous mass on coagulation.

Mineral level of milk:

Addition of calcium or magnesium chloride produces a hard chhana whereas sodium chloride, sodium citrate and sodium acetate have negligible effect on the body and texture of chhana,

Type of coagulants:

Coagulants generally added are organic acids like citric acid, lactic acid or their salts, lemon juice or sour whey. Lactic acid (0.5-0.75%) tends to produce a granular texture chhana suitable for rosogolla making, while citric acid (1-2%) produces doughy product suitable for sandesh making. Calcium lactate (4%)

produces soft body, smooth texture, and pleasant flavour chhana that is suitable for the preparation of sandesh. Generally low acid strength coagulant results a soft body and smooth texture required for rosogolla preparation and high acid strength results a comparatively hard body and less smooth texture required for sandesh preparation.

Coagulation temperature:

Temperature of coagulation exerts a significant influence on physico-chemical attributes. A temperature range of 80-85°C and pH 5.4 for cow milk and 70-80°C and pH 5.7 for buffalo milk will give better yield and quality. Higher coagulation temperature results hard, granular and graininess texture chhana and lead to lower moisture content but higher percentage of milk solids comprising fat, protein, lactose and ash. The lower temperature imparts in a sticky chhana with slow drainage problem.

Stirring/agitation:

Generally slow stirring is preferred for avoiding foam formation and reduce the shattering of the coagulation mass, whereas fast stirring reduce the moisture content and increased hardness in chhana. Again, delayed straining produced comparatively a soft body and smooth texture with higher yield chhana than immediate straining. Delayed drainage of whey following coagulation results in a softer body and smoother and sticky and less chewy texture and is more acceptable from overall quality.

Proteolysis:

Proteolysis of buffalo milk with enzyme trypsin coagulation produced a chhana with very soft and smooth body having minutes sized micelles and suitable for rosogolla preparation. Addition of 0.3% sodium citrate to buffalo milk produces a chhana similar to cow milk chhana. A mixture of 75% buffalo milk and 25% cow milk produces suitable chhana, which offers good rosogolla.

Post manufacture chemical reactions occurring during storage of chhana considerably alter its physico-chemical attributes and render it unfit for consumption. Shelf life of the product packaged in vegetable parchment paper was 2, 3 and 12 days at about 37°C, 24°C and 7°C, respectively. The storage temperature guides the character of spoilage. At low temperatures, there is a heavy growth of moulds on the surface together with the development of a stale flavour; on the other hand at high temperatures the stored product develops a

sour smell and bitter taste together with moulds growth on the surface of chhana.

Fermented milk product:

Fermented Milk is a milk product obtained by fermentation of milk, which may have been manufactured using other permitted raw material, by the action of suitable microorganisms and resulting in lowering of pH with or without coagulation (iso-electric precipitation). Fermented milk may be heat treated after fermentation. The raw material used shall be subjected to a heat treatment as defined in the General Standard for Milk and Milk Products.

Fermented milk products:

<i>Dahi (Curd)</i>	Lactic acid bacteria
Yoghurt	Symbiotic cultures of <i>Streptococcus thermophilus</i> and <i>Lactobacillus delbrueckii</i> sub sp. <i>bulgaricus</i>
Alternate Culture Yoghurt	Cultures of <i>Streptococcus thermophilus</i> and <i>Lactobacillus species</i>
Acidophilus milk	<i>Lactobacillus acidophilus</i> .

Dahi

Definition:

According to FSSA (2006), dahi or curd is the product obtained from pasteurized or boiled milk by souring, natural or otherwise, by a harmless lactic acid or other bacterial culture. Dahi may contain additional cane sugar. Milk solids may also be used in preparation of this product. It should have the same percentage of fat and SNF as the milk from which it is prepared. When dahi or curd other than skimmed milk dahi, is sold or offered for sale without any indication of the class of milk, the standard prescribed for dahi prepared from buffalo milk shall apply.

The dahi may be classified into various types depending upon the type of milk used such as whole milk dahi, skim milk dahi and on basis of acidity and addition of sugar it can be classified as: sweet dahi (acidity < 0.7%), sour dahi

(acidity > 0.7%) and sweetened dahi .The composition of dahi depends upon the type of milk and the manufacturing condition.

Type of dahi preparation:

1. Household preparation

During preparation of dahi at home, cow or buffalo or mixed milk is boiled or simmered for a long time to concentrate it, allow cooling to room temperature and then transferred to earthenware pots or pan. A small amount of the previous day's curd is added as a starter culture and then allowed to set undisturbed overnight. The dahi is usually ready within 16 to 20 hours.

2. Commercial preparation

Fresh, sweet, good quality milk (cow or buffalo or mixed) is received. It is then standardized to have 4-5 percent fat and 10-12 percent solids not fat, preheated to 60°C and homogenized at a pressure of around 176 kg/sq. cm. The milk is preheated to 80°C to 90°C for 15 to 30 minutes, cooled to 40 – 45°C and inoculated with 1 to 2 percent of specific starter culture. It is then filled in a suitable containers using automatic filling and sealing machine and incubated at 40 -42°C till curdling (3-4 hour). When a firm curd is formed, dahi cups are stored in a cold room temperature.

Biochemical Changes

1. Break down of lactose:

Hydrolysis of lactose to glucose and galactose by starter organism is the first step in the process of fermentation during the preparation of dahi. The liberated glucose is then enters the classical Embden Meyer Hoff pathway (EMP). But the galactose produced cannot enter the EMP pathway directly but follows a longer route and ultimately enter the EMP pathway via glucose – 1 – phosphate. Each of the simpler sugar is further acted upon by several enzymes successively before arriving at the lactic acid stage. There may be several form of acid end product. The amount of lactic acid produced may range from 75 – 95 % of the total acidity, the rest being volatile acid.

2. Role of lactic acid:

The lactic acid cause at first an acid flavour combine with calcium of casein to form calcium lactate, then setting free the casein and coagulated it when isoelectric point (4.6) is reached . The fermentation is accompanied by gelling of the solids, principally the proteins and syneresis manifested by appearance of thin exudates of clear whey on the surface of dahi

3. Nitrogen content:

Total nitrogen content of milk remains more or less unchanged during fermentation. Appreciable changes occur in non-protein nitrogen, albumin nitrogen, ammonia and dialyzable nitrogen during fermentation. The increase in the non-protein nitrogen during fermentation is attributed to the breakdown of protein.

4. Salt content:

Considerable changes occur in the mineral contents of milk. The total mineral content is not affected. The soluble calcium and phosphorus are increased during souring. Citric acid completely disappears during fermentation.

5. Vitamin content:

Vitamin content of dahi depends on the type of organisms used for fermentation. Fermentation of milk with *Streptococcus lactic* and *Streptococcus cremoris* results in increase in thiamine, riboflavin and folic acid and decrease in vitamin A. The incorporation of *Propionibacterium shermani* in lactic culture would enrich it with riboflavin and folic acid and cyanocobalamin (vitamin B₁₂). Fermentation of milk with *Streptococcus cremoris*, *Streptococcus diacetylactis*, *Streptococcus thermophilus* and *Lactobacillus thermophilus* results in increase in riboflavin and folic acid and decrease in nicotinic acid.

6. During fermentation, the electrical charge on the fat particles is neutralized, causing the globule to coalesce and rise to top. The iso-electric point (pH 4.5 – 4.6) of the fat globule in milk is slightly higher than that of washed globule (pH 4.3) from cream. With respect to acidity, a pure culture is able to neutralize the charge on the fat globule at a lower level (1%) of acidity than a mixed starter (1.3 – 1.5 %).

Misti Doi

In the eastern region of India, sweet variety of dahi known as Misti dahi, lal dahi or payondhi is popular. It is creamish to light brown colour, firm consistency, smooth texture and pleasing aroma. It is produced with the addition of 6 -6.5% sugar to milk either during boiling or at the setting stage. Prolong heating of sweetened milk at low temperature leads to milk solid concentration and development of brown colour. It is then cooled, add dahi culture and poured into earthen cups and left undisturbed overnight for fermentation. When a firm body curd has set, it is stored at low temperature of about 4°C and served chilled.