Chapter 2

REVIEW OF LITERATURE

Milk is a translucent white liquid produced by the mammary glands of mammals. It provides the primary source of nutrition for young mammals before they are able to digest other types of food. The early lactation milk is known as colostrum, and carries the mother's antibodies to the baby. It can reduce the risk of many diseases in the baby. The exact components of raw milk vary by species, but it contains significant amounts of fat, protein and calcium. In addition to cattle, the milk of buffalo, goat, sheep and yak is used in our country by humans for manufacture of dairy products. In the Western world today, cow's milk is produced on an industrial scale and is by far the most commonly consumed form of milk. The largest producers of dairy products and milk today are India followed by the United States, Germany, and Pakistan (www.fao.org).

As the largest single dairy producing country, India's output continues to grow strongly in the 3-4 percent range, largely in response to internal demand growth and sustained by increasing productivity (Gupta, 2007). India accounts for over half the total milk output of Asia. India is located amidst major milk deficit countries in Asia and Africa. Major importers of milk and dairy products are Bangladesh, China, Hong Kong, Singapore, Thailand, Malaysia, the Philippines, Japan, UAE, Oman, and other gulf countries, all located close to India. There is vast potential for the export of dairy products, the cost of milk production in India being the lowest. Given recent high international prices, India has started to enter certain export markets; particularly for skimmed milk powder. Indian companies like Nestle, Amul, Varshney Bhandu Pvt. Ltd., Harbansh Lal Foods, Shree Vinayak Ingredients, etc. manufacture and export
skimmed milk powder. The major factor influencing production and export of milk products would be the newer uses that may be developed through R&D support. Milk proteins are being utilized increasingly replacing animal and vegetable proteins in special bakery products and instant foods. Through the application of membrane process, milk proteins isolates are being produced. There is scope for introducing newer plants adopting newer processes by the dairy industry in the country.

2.1 Constituents of Milk

The major constituents of milk are: water, fat, protein, lactose, ash or mineral matter. The minor constituents are: phospholipids, sterols, vitamins, enzymes, pigments, etc.

2.1.1 Water

Water is the medium in which all other components of milk are dissolved or suspended. Water content varies from 83.18 to 87.3% in milk of different species. A small percentage of water in milk is hydrated to lactose and salts, while some portion is bound with proteins (Aneja et al., 2002).

2.1.2 Fat

Milk is an emulsion or colloid of butterfat globules within a water-based fluid. Each fat globule is surrounded by a membrane consisting of phospholipids and proteins; these emulsifiers keep the individual globules from joining together into noticeable grains of fat and also protect the globules from the fat-digesting activity of enzymes found in the fluid portion of the milk. The fat-soluble vitamins A, D, E and K are found within the milk fat portion of the milk (Harold, 1984). The average size of fat globules in buffalo milk is larger (4.15 to 4.60 μm) than that of cow milk (3.36 to 4.15 μm).
2.1.3 Proteins

The largest structures in the fluid portion of the milk are casein protein micelles: aggregates of several thousand protein molecules, bonded with the help of nanometer-scale particles of calcium phosphate. Each micelle is roughly spherical and about a tenth of a micrometer across. There are four different types of casein proteins, and collectively they make up around 80% of the protein in milk, by weight. Most of the casein proteins are bound into the micelles. There are several competing theories regarding the precise structure of the micelles, but they share one important feature: the outermost layer consists of strands of one type of protein, k-casein, reaching out from the body of the micelle into the surrounding fluid. These kappa-casein molecules all have a negative electrical charge and therefore repel each other, keeping the micelles separated under normal conditions and in a stable colloidal suspension in the water-based surrounding fluid (Fox and McSweeney, 1998). Caseins are heat stable. Heat has little or no effect on casein molecules since they exist naturally in an open and extended state at higher temperatures.

Pandya and Haenlin (2009) have reported that as compared to cow milk, buffalo milk is richer in total proteins, particularly casein and whey proteins. However, the proportion of various protein fractions is similar in milk of both species. Distinct differences exist in the physico-chemical make up of casein in buffalo and cow milk. The buffalo casein micelle is more opaque, about three times, when suspended in a different medium, than cow milk micelle. Buffalo casein has superior whitening as compared to cow casein due to a higher proportion of calcium present in it.
According to Walstra et al., (1999) milk contains dozens of other types of proteins beside the caseins. They are more water-soluble than the caseins and do not form larger structures. Because these proteins remain suspended in the whey left behind when the caseins coagulate into curds, they are collectively known as whey proteins. Whey proteins make up approximately twenty percent of the protein in milk, by weight. β-Lactoglobulin, α-lactalbumin and proteose-peptone are the most common whey protein by a large margin.

2.1.4 Carbohydrates

Lactose, also called as milk sugar, is the major carbohydrate of milk. The carbohydrate lactose gives milk its sweet taste and contributes approximately 40% of whole cow's milk's calories. Lactose is a disaccharide composite of two simple sugars, glucose and galactose. Buffalo milk usually contains lactose in the range of 4.7-5.0%, while cow milk has slightly lower amount of lactose in the range of 4.5-4.8%. Lactose has only 16-33% of the sweetening power of sucrose. Varman and Sutherland (2001) have explained that lactose makes a major contribution to the colligative properties of milk, such as, osmotic pressure, freezing point depression and boiling point elevation. Lactose finds use as food ingredient due to protein stabilizing properties and low relative sweetness. Lactose may also be used as partial replacer of sucrose in icing and toppings to improve mouth-feel without excess sweetness. It is also added to bakery products such as biscuits to impart controlled degree of Maillard browning, a reaction considered undesirable in many foods. Lactose is a significant source of dietary energy and may promote calcium absorption (www.lactose.com).
Both the fat globules and the smaller casein micelles, which are just large enough to deflect light, contribute to the opaque white color of milk. De (1980) described that the fat globules contain some yellow-orange carotene, enough in some cattle breeds, such as, Guernsey and Jersey cattle, to impart a golden or "creamy" hue to a glass of milk. The riboflavin in the whey portion of milk has a greenish color, which sometimes can be discerned in skimmed milk or whey products. Harold (1984) suggested that fat-free skimmed milk has only the casein micelles to scatter light, and they tend to scatter shorter-wavelength blue light more than they do red, giving skimmed milk a bluish tint.

Milk is valued commercially for its two important parameters, the Milk Fats (F) and the Solids-Not-Fat (SNF). The SNF largely consists of proteins, lactose and minerals. These solids are also referred to as ‘serum solids’. These two parameters usually form the basis for the basis of payment to milk producers in our country. The term ‘Total Solids’ (TS) refers to the quantity of SNF plus fat present in milk. It may range from 12 to 17% depending on its source. Milk of different animal species differs widely in composition. All milks contain the same kind of constituents, but in varying amounts. Factors such as the type of protein; the proportion of protein, fat, and lactose; the levels of various vitamins and minerals; and the size of the butterfat globules, and the strength of the curd are among those that may vary. Aneja et al. (2002) has reported the average composition of cow and buffalo milk, which is summarized in Table 2.1 given below.
Table 2.1. Composition of cow and buffalo milk

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Cow milk</th>
<th>Buffalo milk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water, %</td>
<td>86.50</td>
<td>83.18</td>
</tr>
<tr>
<td>Fat, %</td>
<td>4.39</td>
<td>6.71</td>
</tr>
<tr>
<td>Protein, %</td>
<td>3.30</td>
<td>4.52</td>
</tr>
<tr>
<td>Lactose, %</td>
<td>4.44</td>
<td>4.45</td>
</tr>
<tr>
<td>Total solids, %</td>
<td>13.50</td>
<td>16.82</td>
</tr>
<tr>
<td>Solids Not Fat, %</td>
<td>9.11</td>
<td>10.11</td>
</tr>
<tr>
<td>Ash, %</td>
<td>0.73</td>
<td>0.80</td>
</tr>
<tr>
<td>Calcium, %</td>
<td>0.12</td>
<td>0.18</td>
</tr>
<tr>
<td>Magnesium, %</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Sodium, %</td>
<td>0.05</td>
<td>0.04</td>
</tr>
<tr>
<td>Potassium, %</td>
<td>0.15</td>
<td>0.11</td>
</tr>
<tr>
<td>Phosphorous, %</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Citrate, %</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>Chloride, %</td>
<td>0.10</td>
<td>0.07</td>
</tr>
<tr>
<td>Ca : P Ratio</td>
<td>1.20</td>
<td>1.80</td>
</tr>
</tbody>
</table>

2.2 Buffalo Milk versus Cow Milk

The share of buffalo milk production to the world dairying by Asia is 96.79%. India is the top and recognized player in buffalo milk production followed by Pakistan, China and Italy. It is proudly said that these buffaloes form the back bone of dairying in India and the term “milk” in India refers to that from either cow or buffalo or a combination of these two but the PFA act (1955) says that milk sold without any qualification shall be considered as buffalo milk. (www.dairyforall.com/milk-buffalo.php). Buffalo milk is superior for processing as well as for manufacture of a large number of dairy products, both western and traditional.

Buffalo milk like cow milk is composed of similar constituents but distinctly differs in the level of these constituents. These differences have been fully exploited.
to the advantage of all-producers, processors and consumers. Many workers have reported the compositional aspects and the salt balance of buffalo milk. Sindhu (1996) and Pandya (2007) have reviewed the differences in the two milk with regard to qualitative and quantitative aspects of various milk constituents.

2.2.1 Compositional aspects

2.2.1.1 Milk Proteins

According to Sindhu (1998) buffalo milk has about 11.42% higher protein than cow milk. The concentrations of both, the casein and whey proteins are different in cow and buffalo milk. Buffalo milk contains higher caseins and whey protein than cow milk. Whole of the caseins in buffalo milk is present in micellar form while in cow milk only 90-95% is the miceller casein and rest is present in the serum phase. The particle size of the buffalo miceller casein is larger at 110-160 nm than that of cow miceller casein 70-110 nm (Saraswat, 1985; Oommen and Ganguli, 1973). The voluminosity of the buffalo milk casein is 2.68-3.72 ml/g at 25-27°C, while that of cow milk casein is 4.18 ml/g. Ahmed (2008) observed that the hydration (solvation) of buffalo casein is lower as compared to casein of cow milk. Kuchroo and Malik (1976) quantified the solvation (hydration) of casein micelles from buffalo milk as 2.60-2.90 g water /g casein compared to 3.48 g water/g casein for cow milk. Ahmad (2008) investigated the modifications of protein-protein and protein-minerals interactions in alkaline pH resulting in miceller disruption in cow and buffalo milk and found that the dissociations took place at pH 9.7 and 8.6 for buffalo and cow milks, respectively. These differences were due to higher concentrations of casein and minerals in buffalo than in cow milk. Animal bioassays have shown the Protein Efficiency Ratio (PER) value of buffalo milk proteins to be 2.74 and that of cow milk as 2.49 (Pandya, 2007). By virtue of higher opacity of casein micelles coupled with
higher levels of colloidal protein, calcium and phosphorous, buffalo milk is more densely white and has superior whitening properties as compared to cow milk (Kuchroo and Malik, 1976).

2.2.1.2 Whey proteins

The average range of whey proteins in buffalo milk is found to be between 0.70-0.74% as compared to 0.50-0.53 in cow milk. The average level of proteose-peptone in buffalo milk is 330.5 mg/100ml which is significantly higher than that in cow milk which is 240 mg/100ml (Aneja et al., 2002). Whey proteins of buffalo milk are more resistant to heat denaturation as compared to the cow milk proteins. Dried milk products prepared from buffalo milk exhibit higher levels of undenatured proteins when processed under similar conditions. In general, the reconstitution behavior of dried milk products made from buffalo milk is indistinguishable from those made from cow milk. However, dried buffalo milk may be preferred over dried cow milk for those technological applications where higher levels of undenatured whey proteins would be more desirable.

2.2.1.3 Milk lipids

Sindhu (1998) reported that buffalo milk fat contains higher proportion of high melting triglycerides (9-12%) than cow milk (5-6%) and as a result it is more solid in nature. Similarly, the proportions of butyric acid containing triglycerides are also higher in buffalo milk (50%) compared to only 37% in cow milk (Ramamurthy, 1976). As a consequence of higher proportions of butyric acid containing triglycerides the emulsifying capacity of buffalo milk fat is superior to cow milk fat. Fat globules are bigger (4.15-4.6 μm) in buffalo milk compared to cow milk (3.36-4.15 μm). Buffalo milk is poor in free fatty acids (0.22%) than cow milk fat (0.33%). Similarly phospholipids content of buffalo milk is also less (21 mg/100ml) compared to cow milk (37.37 mg/100ml) (Bector, 2002).
2.2.1.4 Milk salts

Concentration of calcium and magnesium is higher in buffalo milk as compared to cow milk, whereas, the concentration of sodium, potassium and chloride is similar. The content of colloidal calcium and magnesium in buffalo milk is 160 mg and 90 mg respectively per 100 ml of buffalo milk compared to only 80 and 30 mg respectively per 100 ml of cow milk. The Ca/P ration in buffalo milk is 1.8 and it is 1.2 in cow milk (Sindhu, 1998).

2.2.1.5 Other constituents

Lipase and alkaline phosphatase activity is less in buffalo milk (Kumar and Bhatia, 1994). The free amino acids are present in higher concentrations in buffalo milk (0.44%) compared to cow milk (0.15%).

2.2.2 Physico-chemical properties

Sindhu (1998) reported that buffalo milk has higher specific gravity (1.0323 at 20°C), viscosity (2.245 cP at 27 °C) and surface tension (45.50 dynes/cm at 20 °C) compared to the respective values of cow milk as 1.0317 at 20°C, 1.450 cP at 27 °C and 42.50 dynes/cm at 20°C. Similarly it has higher acidity (0.16% as lactic acid), pH (6.7 at 20°C), oxidation-reduction potential (+0.310 volts) as compared to the respective values of cow milk 0.15% (as lactic acid), pH 6.6 at 20°C and oxidation-reduction potential of +0.258 volts. Thermal conductance of buffalo milk is 0.569 kcal / h m °C at (37 °C) which is higher than that of cow milk 0.460 kcal/h m°C at 37°C. The heat stability of buffalo milk (32.28 min at 130°C) is similar to the heat stability of cow milk (31.82 min. at 130°C). Owing to differences in physical properties, milks from two species behave differently when processed for the manufacturing of various products.
2.2.3 Milk products

All the products that can be made from cow milk can be made from buffalo milk. However, there could be some limitations owing to inherent differences in the compositional and physico-chemical properties between cow and buffalo milk (Sindhu, 1996).

2.2.3.1 Cheese

Zicarelli (2004) reported that cheese made from buffalo milk displays typical body and textural characteristics. More specifically, where chewing and stringing properties are specially desired as in the case of Mozzarella cheese, buffalo milk is technologically preferable over cow milk. In Italy, recently legislation has been introduced to restrict use of term "Mozzarella" only to those products exclusively made from buffalo milk (without admixture with cow milk). Certain traditional cheese varieties, such as paneer in India or pickled cheeses from the Middle-East countries, are best made from buffalo milk. As per Upadhyay (1996) the yield of buffalo milk Cheddar, Swiss, cottage and Mozzarella cheese is higher. The sensory qualities of buffalo milk Mozzarella cheese are superior. Zicarelli (2004) reported that inspite of its higher fat percentage, milk and mozzarella cholesterol content is lower for buffalo milk than for cow’s milk (275 mg vs 330 mg and 1562 mg vs 2287 mg respectively). In countries where buffalo milk predominates, several cheese varieties that were earlier made using cow milk are now being manufactured using buffalo milk. An emerging market for buffalo milk cheeses in Western Europe has given a new dimension to the buffalo milk cheese industry (Kanawjia, 1996).

2.2.3.2 Fat-rich dairy products

Due to high fat content and larger fat globule, the cream separation and churning of butter is more facilitated in buffalo milk. The recovery of fat is also
higher as compared to cow milk. The emulsifying capacity of buffalo milk fat is better due to a higher proportion (50%) of butyric acid-containing triglycerides compared to only 37% in cow milk. Therefore, the yield of butter and ghee from buffalo milk is higher (Gokhale et al., 2001).

2.2.3.3 Concentrated and dried products

Pandya (2007) reported that the technologies are being developed for manufacture of variety of condensed and dried milk products using buffalo milk. In addition to regular products, some of the processes have been developed for making dehydrated and formulated products like dried cream, khoa powder, chocolate milk powder, etc., using buffalo milk. Higher proportion of beta casein in buffalo milk makes it easier to prepare humanized milk. With the advancement of technology, it is now feasible to prepare infant milk food from buffalo milk that reasonably corresponds to human milk with respect to its composition.

2.2.3.4 Health foods

The presence of higher levels of various bioprotective factors, such as immunoglobulins, lactoferrin, lysozyme, lactoperoxidase as well as bifidogenic factors, render buffalo milk more suitable than cow milk for the preparation of a wide range of special dietary and health foods (Rajput, 2007).

2.2.4 Nutritive value

There is practically no difference in the nutritive value and digestibility of milk and milk products obtained from cow and buffalo milks. Buffalo milk contains all the nutrients in higher proportions than cow milk. Higher total solids in buffalo milk provide more calories per unit weight, that is, 100 calories per 100g of buffalo milk compared to 70 calories per 100g of cow milk. Significantly, cholesterol content
of buffalo milk is 275 mg/100 g as compared to the corresponding value of 330 mg/100 g for cow milk. Buffalo metabolizes all the carotene into vitamin A, which is passed on to milk as such. Buffalo milk is also superior to cow milk in terms of important minerals, namely calcium, iron and phosphorus which are higher by 92, 37.7 and 118%, respectively, than those present in cow milk which makes it better nutritional material (Sahai, 1996).

2.2.5 Commercial viability

According to Pandya (2007), buffalo milk is commercially more viable than cow milk for the manufacture of fat-based and SNF-based milk products, such as butter, ghee and milk powders, because of its lower water content and higher fat content. Most significantly, the lower cholesterol value should make it more popular in the health conscious market. Unlike the cow milk which is pale-creamish yellow in colour and cow milk fat which is golden yellow in colour, buffalo milk is distinctively whiter. UHT-processed buffalo milk and cream are intrinsically whiter and more viscous than their cow milk counterparts, because of conversion of greater levels of calcium and phosphorus into the colloidal form. Buffalo milk is, therefore, more aptly suitable for the production of tea and coffee whiteners than cow milk. Higher innate levels of proteins and fat render buffalo milk a more economical alternative to cow milk for the production of casein, caseinates, whey protein concentrates and a wide range of the fat-rich dairy products.

Buffalo milk commands a premium price from collection centers linked to rural based farmers. Full cream buffalo milk is sold at a premium price because of its flavour and ability to produce good quality product. Large sized fat globules and higher proportion of solid fat in buffalo milk facilitates cream separation and churning of butter. The percentage of fat harvested from buffalo milk is significantly higher
when compared to cow milk. The competitive advantages of buffalo milk, therefore, needs to be fully exploited for value addition and developments of new products with special attribute.

### 2.3 Milk Powder

Milk powders are made by evaporating water from milk to dryness. One purpose of drying the product is to preserve it; dried product has a far longer shelf life than liquid milk and due to its low moisture content it does not need a refrigerated storage. Another purpose is to reduce its bulk for economy of transportation. Dried milk products include such items as dry whole milk, non-fat dry milk, dry buttermilk, dry whey products and dry dairy blends. These powdered milk products are usually made by spray drying nonfat skim milk, whole milk, buttermilk or whey. Pasteurized milk product is first concentrated in an evaporator to about 40-50% total solids. The resulting concentrated product is sprayed into a heated chamber where the water almost instantly evaporates, leaving fine particles of powdered solids. The ultimate aim is to obtain dry product, which, when recombined with water, give little or no evidence of detrimental change compared to the original liquid product (Walstra, 1999). Dry milk provide a means of handling the excess milk supply during a flush season, while in lean season, that meant the diversion of dry milk for production of liquid milk. Thus, dry milk may be called as the balance wheel of dairy industry. In India, the first ever commercial production of spray dried milk was started by AMUL dairy, Anand, in 1955. Since then, it registered a steady growth and the annual skim milk production in India in the year 2005 was 0.52 million tonnes valued at ₹ 46.8 billion. It is estimated to grow up to 0.7 million tonnes valued at ₹ 91 billion by the year 2011 (Gupta, 2007).
2.3.1 Composition of milk powder

Dried milk or milk powder is the product obtained by the removal of water from milk by heat or other suitable means, to produce a solid containing 5% or less moisture. The dried product obtained from whole milk is called Whole Milk Powder (WMP) and that from skim milk is known as Skim Milk Powder (SMP). According to BIS standard: IS: 1165-1967, the specifications for dried milks are given in the Table 2.2.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Requirements for</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Whole milk powder</td>
</tr>
<tr>
<td>Flavour and odour</td>
<td>Good</td>
</tr>
<tr>
<td>Moisture, % by wt. Min.</td>
<td>4.0</td>
</tr>
<tr>
<td>Total milk solids, % by wt. Min.</td>
<td>96.0</td>
</tr>
<tr>
<td>Solubility index, ml</td>
<td></td>
</tr>
<tr>
<td></td>
<td>If roller dried</td>
</tr>
<tr>
<td></td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>If spray dried</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td>Solubility, % by wt. Min.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>If roller dried</td>
</tr>
<tr>
<td></td>
<td>85.0</td>
</tr>
<tr>
<td></td>
<td>If spray dried</td>
</tr>
<tr>
<td></td>
<td>98.5</td>
</tr>
<tr>
<td>Total Ash, % by wt. Max. (on dry basis)</td>
<td>7.3</td>
</tr>
<tr>
<td>Fat, % by wt.</td>
<td>Not &lt; 26.0</td>
</tr>
<tr>
<td>Titrable acidity (as L.A. %) Max.</td>
<td>1.2</td>
</tr>
<tr>
<td>Bacterial count per g. Max.</td>
<td>50,000</td>
</tr>
<tr>
<td>Coliform count per g. Max.</td>
<td>90.0</td>
</tr>
<tr>
<td>Yeast and mold count per g. Max.</td>
<td>10.0</td>
</tr>
</tbody>
</table>
Under modern drying methods, the nutritive value of milk is preserved to a great extent, while there is slight loss of lysine due to heat treatment. Dry whole milk is good source of vitamin A, calcium, phosphorous and riboflavin.

2.3.2 Process for manufacture of milk powder

Milk powder is prepared by the processes of concentration and drying of milk. Concentration is achieved by evaporating part of the water of whole milk or skim milk in an evaporator. Drying is removal of water from concentrated milk to the extent of leaving its solid content in a completely or nearly moisture free state. Milk and milk products are dried by either the roller process or spray process, the spray process dominates today (Kessler, 1981).

2.3.2.1 Evaporation

When the milk receives enough energy in the form of heat, its water molecules escape as vapour. The rate at which the water molecules escape depends on various factors, viz., temperature of milk, temperature of surroundings, the pressure above the milk surface and rate of heat transfer. If the space above milk surface is closed, the evaporation will continue until the air is saturated with water molecule. Removal of moisture by evaporation is enhanced by adding heat and removing the saturated wet air above milk surface. This is done by forcing air or by decreasing the pressure above the milk surface in an evaporator.

Evaporator is an equipment in which milk is treated for removal of moisture to obtain an intermediate or end product. Evaporators are widely used for preconcentration of feeds for use in conventional commercial drying processes. The usual practice for milk and other heat sensitive products is to operate the evaporators at a vacuum so that the temperature of boiling and evaporation is lower. With lower
temperature of evaporation there is less heat damage to product. Heating is indirect by means of steam which condenses on one side of the partition. The heat is then transferred through the partition wall to the product on other side. From an operational point of view, the equipments used in evaporators perform the following operations:

i) Flow of liquids: pumping of feed, steam condensate, make up water.
ii) Heat transfer: heat exchangers in evaporators, condensers, pre-heaters.
iii) Vapour removal: pumps for maintaining the vacuum in evaporators.
iv) Vapour liquid separation by entrainment separators.

Milk evaporation plants comprise mainly the milk heater, vapour separator, condenser, milk discharge pump and vacuum pump. Although all the evaporators generally work on the same principle, they differ in design. The tubes which form the partition can be horizontal or vertical and the circulation of heating medium can be either inside or outside the tubes. The natural circulation evaporator, also known as climbing film evaporator, milk is brought to boil in tubular heat exchangers (calendrias) consisting of large number of tubes through the product rises. The tubes are externally heated by stem chest. The milk enters the bottom of calendrias and product is discharged from the top. The tube length is usually 4 m and diameter 25 mm. To reduce the amount of heat treatment falling film evaporators are used, in which the milk is introduced at the top and discharges from the bottom. The product from the calendrias is discharged in to vapour separator, where the vapours are removed from the product (Robinson, 1994).

The vapour produced through evaporation contains a considerable amount of latent heat. This vapour may be used as a heat source in another evaporator, commonly called second effect evaporator. This method is feasible if the second
effect is operated at a lower pressure than the first, so that a positive value of temperature difference is obtained across the stem chest surface in the second effect. Likewise, more effects could be added to make it multiple-effect evaporation. A common multiple-effect evaporator is the triple effect system; however, evaporators up to seven effects are now used in dairy industry (Verma, 2000). Multiple effect evaporators may be connected in a variety of ways, such as, forward feed, backward feed or mixed feed system. In a single effect evaporator, the steam consumption per kg of water evaporation is 1.0 to 1.2 kg; in double effect evaporator it reduces to 0.6 kg; in triple effect evaporators it is further reduced to 0.4 kg. The choice of number of effect will be dictated by an economic balance between the savings in steam and the added investment costs brought about by increasing the number of effects. High heat economy is obtained by recompression of vapour generated by boiling of milk. This is done by adding energy to the vapour, either by steam jet in a thermal vapour recompression (TVR) system or by a compressor in a mechanical vapour recompression (MVR) system.

2.3.2.2 Drying

The removal of water from a feed to the extent of leaving its solids content in a completely or nearly moisture free state is termed as drying. Milk and milk products are dried by either the roller process or spray process.

Roller drying

Roller drying, invented in 1902 by John A. Jost of USA, was the first method used for drying milk and milk products. The principle of the roller drying process is that the milk or milk product to be dries is applied in a thin film upon the smooth surfaced, internally steam heated and rotating metal drum. The film of the dried
product is continuously scrapped off by a stationary knife or doctor blade, located opposite in the point of application of milk. The dried milk film thus obtained is ground, which is then sifted, packed and stored. Roller drier may consist of single or double drum, having either trough feeding from the top or the pan feeding from the trough below. Drums may operate with atmospheric pressure or vacuum around the product. The double drum atmospheric drier is one most commonly used in the dairy industry.

According to Ahmad (1997), the drums used for drier are 60 to 120 cm in diameter and up to 360 cm in length. The drums are carefully machine, inside and outside, so that the thickness throughout the length is same. The spacing between the drums affects the film thickness; it is usually kept between 0.5 to 1.0 mm. The speed of the drums is adjustable from 6 to 24 RPM. Speed is important as it affects the thickness of milk film and the time of solid contact with metal. The speed of the drum depends upon the concentration of milk and the final moisture content. Both drums turn at the same speed. The inside of the drum is heated with steam at 3.0 – 6.0 kg/cm$^2$ and the drum temperature below 130°C is suggested. The time that the solid is in contact with metal is 3s or less. The product is removed after $\frac{3}{4}$ to $\frac{7}{8}$ of a revolution of the drum has taken place. The ‘doctor blade’, a sharp hard flexible knife, positioned at angle of 15 to 30° with the surface, scrapes the dried material from the drum. The conveyor for each drum discharges the product in to elevators and then for sizing the dried product. The dried milk film thus obtained is ground, which is then sifted, packed and stored.

**Spray drying**

Spray drying is a process in which instantaneous removal of moisture from a liquid takes place. To achieve this, the liquid to be dried is converted into a fog like
mist by atomization, where by it is given a large surface area. The atomized liquid is then exposed to a flow of hot air in a drying chamber. Upon contact with hot air, the moisture evaporates quickly and the solids are recovered as powder consisting of fine hollow spherical particles with some occluded air (Robinson, 1994). From an operational point of view, the equipments used in milk spray drying plant perform the following operations:

a) Dispersion of milk in fog like mist: Rotary or Disc Atomizers.

b) Mixing of the hot fog like mist into a steam of hot air: Drying Chamber.

c) Separation of the dry particle from the drying air: Cyclone Separators.

Spray drying is a gentle method of drying. The material to be dried is suspended in air and drying time is very short. Air inlet temperature could be varied between 170 to 215°C. The temperature in the drying chamber is equal to the air outlet temperature which is approximately 95 °C for single stage and lower for multistage drying. The product temperature is 20-30 °C below the air outlet temperature. Milk is preheated and concentrated to 40-45% percent total solids in a vacuum pan or evaporator. Hot air is filtered and directed in to the drying chamber. The concentrate is atomized to obtain small particles ranging from 10-100m in diameter. The air leaving the drying chamber enters a cyclone separator where the fine particles are collected. The dried products are cooled, sifted and packed in suitable packaging material (Ahmad, 1997). Single-stage drying is most simple installation for making spray dried milk powder. In this removal of all the moisture takes place in the spray drying chamber itself. The subsequent pneumatic conveying system serves only to collect the powder leaving the chamber. In a two stage drying system, the pneumatic conveying system is replaced by a fluid bed dryer which acts
as a second stage drier. The moisture content of the powder leaving the drying chamber is 2-3% higher than the final moisture content. In the first section of fluidized bed powder is dried to its final moisture content by air at 100-120°C and in the second section the powder is cooled by air at 10-15°C.

Atomization covers the process of liquid bulk break-up into millions of individual droplets forming a spray. A cubic metre of liquid forms approximately $2 \times 10^{12}$ uniform 100μm droplets which offer a total surface area of over 60,000 m$^2$. Due to this vast surface are of droplets, the evaporation rate is rapid. The milk must be sprayed into the hot air as nearly as possible uniform in size. The atomization affects the product properties such as air content, moisture content, bulk density, particle size, color and dispersibility (Masters, 1991). There are three methods of atomization: pressure nozzle or single fluid nozzle; centrifugal or rotating disc; and two fluid nozzle atomization. In pressure atomization the concentrated milk is forced through the nozzle orifice of 0.125 mm diameter at a high pressure around 140-210 kg/cm$^2$. The milk swirls out in a cone shaped sheet which breaks up into droplets. In centrifugal atomizer the concentrated milk is fed to an atomizer wheel, rotating at a speed of 6,000-20,000 rpm, Due to the rotation of wheel, the milk is flung out at a high speed through radial channels in the wheel and is atomized into a very fine spray. In two fluid nozzle atomization a stream of compressed air or steam is used to disintegrate the jet of milk.

In most of the dryers main bulk of milk powder collects at the conical base of chamber from which it is removed continuously by mechanical means, such as, rotating discharge valve or a suction blower. The outlet air is then passed through cyclone separators and bag filters for removal of remaining amount of milk powder from it.
2.3.3 Skim milk powder

Skimmed milk powder, also known as fat free dried milk, is the milk powder produced by evaporating the water from the skimmed or 0.5% fat milk by heat treatment. It is a creamy fine powder to feel, white in color. Skimmed milk powder contains almost the same amount of proteins (26%) and carbohydrates (37%) as in the liquid form on dry basis. Skim milk is a source of lactose and casein and other nutrients. Since the fat percentage is decreased to almost nil, skimmed milk powder is deficient in fat soluble vitamins but the proteins, water-soluble vitamins and minerals are preserved. Skimmed milk powder is, therefore, usually fortified with vitamins A and D. Skimmed milk powder can be reconstituted easily by just adding water and can be used as regular milk for drinking or for cooking and incorporated in many recipes.

Skim milk powder is a highly nutritious, versatile, and multi-functional food ingredient with a wide range of applications. It may be used as a food ingredient in bakery, confectionery, dairy, sports and nutrition products, infant formulas, and other consumer products. The foaming and whipping properties of skim milk powder allows this product to work well in ice creams, cakes, dry mixes, mousses, and aerated confections such as malted milk and nougat centered candy. Skim milk powder aids in the formation and stabilization of emulsions, and enhances mouth feel in salad dressings, soups and sauces, dairy beverages, sausages, and sour cream. The thickening, water binding, and gelling properties of this product provides an ingredient suitable for puddings, set yogurts, sauces, and dairy beverages (Edgar Speer, 2005).

Robinson (1994) explained that the conventional process for the production of skim milk powders involves the pasteurizing of milk and separating it into skim milk and cream using a centrifugal cream separator. Surplus cream is used to make butter.
or anhydrous milk fat. Milk is preheated between 75 and 120°C for a few seconds concentrated in an evaporator from initial around 9.0% total solids content up to 40-50% total solids and then spray dried. The concentrated milk may be heated prior to atomization to reduce its viscosity and to increase the energy available for drying. The remaining water is evaporated in the drying chamber, leaving a fine powder of less than 6% moisture content with a mean particle size typically of < 0.1 mm diameter.

Milk powders are more stable than fresh milk but protection from moisture, oxygen, light and heat is needed in order to maintain their quality and shelf life. Milk powders readily take up moisture from the air, leading to a rapid loss of quality and caking or lumping. The fat in whole milk product can react with oxygen in the air to give off-flavours, especially at higher storage temperatures (>30°C) typical of the tropics. Skim milk powder having negligible fat content has less of this problem. Milk powder is packed into either plastic-lined multi-wall bags of 25 kg or bulk bins of 600 kg. Whole milk powder is often packed under nitrogen gas to protect the product from oxidation and to maintain their flavour and extend their keeping quality. Packaging is thus chosen to provide a barrier to moisture, oxygen and light.

2.3.4 Physico-chemical and functional properties of milk powder

Milk powders possess various physico-chemical and functional properties which are important to both industrial and consumer use (Upadhyay, 1989). These properties are the basic elements of quality specifications of milk powders. The properties of powder are affected by the milk quality, the design of evaporator and dryer, and by the process conditions. Physical properties include particle shape, size, moisture content, bulk and particle density, etc. The functional properties include flowability, wettability, sinkability, dispersibility and solubility. All these properties have been discussed in detail in section 2.6 of this chapter.
Good quality milk powder should flow readily, be free from lumps or caking and be uniformly white or light in colour. Dried milk absorbs moisture very rapidly from atmosphere and if packed in materials which are not impermeable to moisture, it may develop large hard lumps or severe caking during storage. A general brown discoloration may develop as a storage defect, mainly when powder with high moisture content is exposed to high temperature. The properties involved in reconstitution of dried milk are wettability and solubility. Wettability affects the speed and ease of solution. Very small particles under 50 µm are difficult to wet and tend to produce lumps which are slow to disperse in water. A particle size in the range 100-150 µm is generally considered to be an ideal size (Jha, 2002).

Loss of solubility is due to denaturation of protein by heat treatment during the manufacturing process (Ranganadham, 1988). The severe heat treatment used in atmospheric roller dying reduces the solubility of the powder, whereas, spray dried milk powder more soluble. The use of temperature above 74°C for preheating the milk reduces the solubility of the powder. Microorganisms do not proliferate in dried milk, and storage defects are purely chemical in nature. These tend to develop slowly and normally the product could be stored for many months. The storage life, is however, influenced by temperature and humidity of storage.

2.4 Dried Casein

Casein is the principal protein found in milk and is responsible for the white, opaque appearance of milk in which it is combined with calcium and phosphorus as clusters of casein molecules, called micelles. The major uses of casein until the 1960s were in technical, non-food applications such as, adhesives for wood, in paper
coating, leather finishing and in synthetic fibers, as well as plastics for buttons, buckles, etc. During the past 30 years, however, the principal use of casein products has been as an ingredient in foods to enhance their physical (so-called functional) properties, such as whipping and foaming, water binding and thickening, emulsification and texture, and to improve their nutrition (Southward, 1994).

Casein exists in milk in complex groups of molecules, referred to as calcium phospho-caseinate, that are called micelles. The micelles consist of casein molecules, calcium, inorganic phosphate and citrate ions, and have a typical molecular weight of several hundred million. The casein micelles exist in milk as a very stable colloidal dispersion. When acid is added to milk, this complex is dissociated. As the pH of milk is lowered the casein begins to precipitate out of solution and the calcium and calcium phosphate are liberated to soluble form.

2.4.1 Types of casein

As per De (1980) there are two basic types of casein - acid and rennet casein. They are named in accordance with the coagulating agent employed.

i) Three types of acid casein are made commercially: lactic, hydrochloric and sulphuric acid caseins. In New Zealand, lactic acid casein has been the most common casein product, although larger quantities of sulphuric acid casein have been produced in recent years. In Australia, Europe and India, the most common precipitant for acid casein is hydrochloric acid, which is a by-product of the chemical industry and hence is relatively cheap. The properties of the different types of acid casein are very similar and, for most applications, the acid caseins can be used interchangeably.
ii) For the manufacture of rennet casein, several different coagulants are now available. These include chymosin (previously known as rennet or rennet extract.), the milk-clotting enzyme extracted from the stomachs of young calves, and a number of so-called microbial rennets, which are enzymes that have been produced by means of microbial fermentation techniques. The caseins produced using any of these enzyme preparations are all known as rennet casein, and all have similar properties. However, their properties are noticeably different from those of acid casein.

2.4.2 Preparation of casein

Fresh, clean, sweet skim milk which is as fat free as possible is used in the preparation of casein. Gupta (1989) has discussed different unit operations involved in manufacture of casein are as below:

2.4.2.1 Precipitation

Casein exists in milk as calcium caseinates and calcium phosphate complex. When an acid is added to milk, this complex is dissociated. At about pH 5.3, the casein begins to precipitate from the solution: and at the iso-electric point of casein, about pH 4.7, maximum precipitation occurs. The casein coagulates as a watery, gel like curd. The gel is broken to allow for the expulsion of water from it. The precipitation of casein involves three considerations: acidity and pH, temperature and the speed at which it is stirred. A little more acid is added after precipitation till a pH of 4.1 is reached in order to dissolve the calcium which flows out with whey. It also helps in improving the texture of the curd and making the washing easier to remove the whey proteins, lactose, salts and acid. De (1980) explained the importance of
temperature during precipitation and its effects the texture of casein. If the temperature is less than 35°C the casein curd is soft and fine and is slow to settle and difficult to wash. If it is between 35-38°C it is coarse and easier to wash. If it is more than 38°C the curd is coarse and lumpy and has a chewing-gum texture.

2.4.2.2 Drainage and washing

The whey from the curd is removed promptly because if the curd is allowed to stay in the whey for longer period then it is difficult to remove impurities from it. So the curd is allowed to settle and whey is drained off immediately. Curd is then washed with cold water twice. In the first washing, the wash water is made slightly acidic and curd is gently stirred during washing.

2.4.2.3 Pressing, shredding and spreading

The wet curd is pressed to remove as much water as possible. Normally it is not possible to reduce the moisture level in the curd to less than 55%. The pressed curd is to be promptly shredded and dried to prevent spoilage by mold and bacterial action. Milled curd of uniform size particles is spread in over standard perforated trays for drying.

2.4.2.4 Drying

Bhadania and Shah (1989) studied the drying of casein curd under controlled humidity and temperature conditions in continuous flow hot air oven. It was recommended that inlet hot air temperature should range between 71-77 °C and outlet air temperature between 52-57°C, in order to avoid the risk of discolouring the casein and impairing its solubility. Once started the drying should not be interrupted till the moisture content is reduced to less than 8%.
2.4.2.5 Grinding

Casein is cooled to room temperature before grinding. Warm casein becomes plastic in the grinder and sticks to it. The fineness of grinding depends on the requirement of the user. Uniformity of size in ground casein is achieved by passing it through screens of a particular size.

2.4.2.6 Packaging and storage

The dried casein is packed in heavy 3-ply paper bags with polythene liners. The filled packages of casein are closed air tight and stored at a dry place maintained at a uniform temperature as wide variations in storage temperature will cause the casein to sweat and mould (Gupta, 1989).

2.4.3 Edible casein

De (1980) has explained the process requirements for manufacture and composition of edible casein. Edible acid casein is the milk product obtained by separating; washing and drying the acid-precipitated coagulate of skimmed milk and/or of other products obtained from milk. Edible acid casein is highly nutritional, low in fat and cholesterol, and flavourful, making it ideal for medical and nutritional applications. It is used in coffee whiteners, infant formulas, processed cheese, and for use in pharmaceutical products. It is the casein which is isolated from skim milk by taking special precautions to ensure its suitability for use in patented food and pharmaceutical preparation. These precautions are connected chiefly with strict control of quality of skim milk, use of standard equipment and technique for production, maintenance of strict hygienic conditions of processing and packaging and storage under approved conditions. The BIS specifications for casein (edible quality) are given in the Table 2.3
### Table 2.3 B.I.S. Standards for casein (Edible quality)

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture, %wt. Max.</td>
<td>10.0</td>
</tr>
<tr>
<td>Total ash, %wt.</td>
<td>2.5</td>
</tr>
<tr>
<td>Acid insoluble ash, %wt. d.b. Max.</td>
<td>0.1</td>
</tr>
<tr>
<td>Fat, %wt.</td>
<td>1.5</td>
</tr>
<tr>
<td>Nitrogen, %wt. d.b. Max.</td>
<td>14.5</td>
</tr>
<tr>
<td>Total acidity in terms of ml of 0.1N NaOH (per g)</td>
<td>6.14</td>
</tr>
</tbody>
</table>

BIS (1965)

Edible casein is prepared on lines similar to those followed for acid casein, with hydrochloric acid, under the special precautions mentioned above. The curd is precipitated at pH 4.1-4.3, followed by three separate washings of curd in waters of proper pH and with contact time of 15-20 min. each. The second washing is with hot water at 71-77°C, which affects pasteurization of curd for reducing bacterial count. Last washing is with neutral water at 41°C.

### 2.4.4 Functional properties of casein

#### 2.4.4.1 Solubility

Acid and rennet casein are insoluble in water. Virtually all applications of casein products require them to be dissolved first. Consequently, before use, acid casein must be dissolved using an alkali to produce a solution with a pH of 6.5 or higher. The caseinates mentioned in the previous sections are used for food and pharmaceutical applications. For non-food, technical applications, acid casein may be dissolved in other alkalis such as borax or ammonia, usually to a somewhat higher pH (7.5-9.5, or higher) than that used for edible applications (Walstra, 1999).
2.4.4.2 Water absorption and viscosity

Casein products can absorb substantial amounts of water, so they can modify the texture of dough or baked products, serve as the matrix former in cheese-type products, produce specialized plastic materials, or increase the consistency of solutions such as soups. They are good film-formers and find use in whipping and foaming applications, and in emulsions of fats or oils in water.

2.4.4.3 Nutrition

As per De (1980), the nutritional quality of a protein is determined primarily by its essential amino acid content. For adult man, eight amino acids are essential, *i.e.* they must be supplied in the diet. These are isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan and valine; the infant requires histidine as well.

In comparison with an ideal reference protein composition that was developed by the FAO in 1973, casein contains an adequate supply of all the essential amino acids with the possible exception of the sulphur-containing amino acids methionine and cysteine.

2.4.4.4 Applications of casein products

The uses of casein products in foods include; bakery, confectionery, cheese products, coffee whiteners and creamers, cultured milk products, high fat powders, shortenings and spreads, ice cream and frozen desserts, infant foods, nutritional food bars, pasta, pharmaceuticals soups and gravies, sports drinks, whipped toppings, etc.

Casein is generally not consumed as a food on its own. Casein products are used mainly as ingredients in foods for the purpose of either modifying the physical properties of that food product or providing nutritional supplementation to it. As a consequence, they usually form a relatively minor proportion of the food.
2.5 Whey Protein Concentrates Powder

2.5.1 Whey

Whey is a liquid left after removal of casein and fat from milk in the manufacture of cheese, paneer, casein, chhana and other coagulated products. Its composition varies according to the type of product from which it is derived. Whey comprises of lactose, protein, fat, minerals and vitamins (Kennedy, 1985).

Sienkiewicz and Riedel (1990) reported that in the production of cheese or casein, about 80 to 90% of original milk used yields whey as a by-product. This whey although contains 50% of all the milk constituents but because of low concentration of these constituents (about 6.4 to 7.0% dry matter), it has not been commonly considered as a by-product but as a waste product. Whey constitutes the most potent of all dairy wastes and strongest waste of any kind. Drainage of whey into streams without prior treatment is not permitted in most of the milk processing countries due to its high BOD value of 30 to 60 g O\textsubscript{2}/l. The disposal of whey thus is of great economic concern to the dairy industry.

Puranik (2001) has described that whey is a highly nutritious by-product of cheese, paneer or casein production. Whey contains 6 to 7% dry matter of which, 70 to 75% is lactose and 14 to 15% is protein. Whey which contains most of the milk sugar and about 20% of milk protein, water soluble vitamins and minerals should play a significant role in human nutrition as a source of energy, protein, vitamins and micronutrients. The whey proteins represent the non-casein proteins as well as the fractions and fragments of the casein which remain soluble when the casein has been precipitated enzymatically by rennet or isoelectrically by acid. Nutritionally, the most valuable whey component is the whey protein, one of the best proteins known.
The high nutritional value of whey proteins is based on its higher concentration of essential amino acids, such as, tryptophan, leucine, isoleucine, threonin and lysine than casein (Renner, 1983). The PER of whey proteins is 3.6 as against 3.8 of whole egg and 2.9 of casein, whereas NPU is 94 for whole egg, 76 for casein and 92 for whey proteins (Renner and Abd El-Salam, 1991). Because of the nutritional significance whey proteins are being used by nutritionists and medical profession by specifying whey products for specialized dietetic needs of geriatric and convalescing patients.

Whey and whey derived products besides being a nutritional ingredient in various foods are also used as functional ingredient supplying flavour, texture, colour and aeration properties in variety of foods (Kinsella, 1985; Morr and Foegeding, 1990). Whey proteins possess very good functional properties, such as, solubility, foaming, emulsifying, gelling and water binding (Patel and Kilara, 1990). Whey protein concentrate powder (WPCs), which contain sufficiently high protein concentrations in a predominantly in denatured form, with minimal lactose and lipid contents, are highly acceptable as functional protein source for food industry. Because of excellent nutritional and functional properties of whey solids, the various food applications include; bread and baked foods, infant and dietetic foods, ice cream and frozen desserts, cereals, soups, sauces, toppings and dressings, snack foods, confectionaries and beverages.

2.5.2 Whey processing

Whey can be utilized in several ways. The processing options for whey fall into four main areas:

i) Those concerned with simple removal of water, spray or roller drying to yield whey powder.
ii) Those concerned with increasing the ratio of protein in the end product, it involves ultrafiltration for manufacture of whey protein concentrate, fractionation processes for the manufacture of protein isolates, heat treatment for the production of lactalbumin.

iii) Those concerned with utilization of lactose in whey, it involves treatment with lactase or heat / acid for lactose-hydrolyzed products.

iv) Those designed to alter the mineral composition of the product, it involves electro- dialysis and ion-exchange for the manufacture of demineralized products.

According to Parekh (2007), an effective method of whey utilization in our country is yet to be undertaken on a large scale. The quantity of whey produced in each plant is not sufficient to utilize it economically. Nevertheless, markets for whey protein, lactose and whey protein concentrate have matured. In deed whey protein concentrates are now considered to be commodity products. It has been estimated that about one million tonne of whey is annually derived as a by-product which possesses about 70,000 tonnes of nutritionally rich solids. Considerable economic benefits can thus be secured from the utilization of whey.

2.5.3 Whey protein concentrate

WPC is the substance obtained by removal of sufficient non-protein constituents from whey so that the finished dry product contains not less than 25% protein (Renner and Abd El-Salam, 1991). The average content of lactose, ash and fat in WPCs with a protein content of 30 to 85% varies significantly (Gupta and Reuter, 1992). The extent of variation of protein, fat, lactose ash and moisture is found to be 30-80, 3-8, 5-55, 4-12 and 2-16%, respectively (Engl, 1982). At a protein
level of 34% of TS, WPC has an approximate composition equal to non fat dry milk; difference lie in mineral profile of the ash content and the type of protein (Zall, 1982).

Most of the whey obtained in western countries is from cheese and casein prepared from cow milk. Composition of indigenously available whey, obtained from cheese, paneer, casein and other products made from buffalo milk varies widely with respect to mineral composition, such as, calcium and phosphorous content and also in the content of various protein fractions.

### 2.5.4 Preparation of WPC

#### 2.5.4.1 Ultrafiltration

Ultrafiltration is a pressure driven membrane process that can be used in separation and concentration of substances having molecular weight between $10^3$-$10^6$ Daltons. The process is being used for fractionation and concentration of aqueous solutions. With the introduction of this technology, it is possible to recover whey in its native form. Ultrafiltration reduces the concentration of low molecular weight substances and increases the relative concentration of protein. It thus achieves the fractionation of whey into protein rich and lactose containing streams. In ultrafiltration process most of the protein is retained and most of the lactose, ash and NPN pass through permeate depending upon operational parameters and cut off value of membrane. The protein lost in permeate is about 0.25 g/l (Barbano et al., 1988). The retention or rejection of various constituents during ultrafiltration is influenced by various operational parameters as well as processing conditions. In the early stage of developments the maximum possible protein could be achieved by ultrafiltration membranes was about 20% (80% on dry matter basis). However, with the new
developments in the area, WPC with very high protein level, up to 80% and low fat is being made by UF processing.

The retention of protein varies with the degree of volume reduction during the process. At the initial stages protein retention is less but as the concentration increases, there is an increase in the retention of protein. At higher concentrations of protein in retentate, the loss of protein in permeate is reported to be high. The rate of permeation of lactose is high in initial stages, but at 50-95% volume reduction, there is a decreasing trend of permeation (Jayaprakasha, 1992). In actual terms, the lactose retention varies from 11.3 to 21.8%. The retention coefficient of minerals is found to be significantly less than other components of whey. With the change in volume reduction the behaviour of minerals with regard to retention is similar to other components. Preheating of whey and UF temperature treatments affect the constituents of retentate and this effect was more pronounced in calcium. A pretreatment of whey to 80°C for 15 s prior to concentration followed by cooling to 50°C and operation of ultrafiltration at 50°C is recommended for maximum permeation per unit area of membrane (Jayaprakasha, 1992).

2.5.4.2 Diafiltration

Diafiltration is a process in which UF retentate is diluted with water and reultrafiltered to effect further fractionation (Renner and Abd El-Salam, 1991). It means that water is added to the retentate thereby the viscosity is reduced and the concentration of lactose, ash and NPN is decreased by further ultrafiltration. By ultrafiltration variation in protein: lactose ratio can be obtained. A maximum of 83.20% (on DM basis was obtained when whey was ultrafiltered followed by two step diafiltration (Tratnik and Krsev, 1991). Thus for the manufacture of end products
with high protein, ultrafiltration followed by diafiltration is recommended. In order to achieve higher protein values more diafiltration steps may be followed.

2.5.4.3 Spray drying

For manufacture of dried whey protein concentrate, the retentate obtained by UF is either concentrated further by vacuum evaporation and dried or it is directly spray dried after UF concentration of whey. An inlet temperature of 180°C and outlet temperature of 80°C is recommended for direct spray drying of UF retentate (Jayaprakasha, 1992). The process of concentration and drying of whey had no significant effect on protein solubility. The spray dried WPC is then cooled to room temperature and packed in polyethylene and metallized polyester packaging materials.

2.5.5 Functional properties of WPC

WPC may be produced with a wide range of functional properties. It is this characteristic that can increase the attractiveness of WPC as a food ingredient. Functional properties have been defined as those physical and chemical properties which affect the behaviour of proteins in the food system during processing, storage, preparation and consumption. Functional properties include: solubility, whippability, emulsification, foaming and heat setting, etc. Although solubility itself is a functional property of proteins, it is also a pre-requisite for other functional properties such as their foaming, emulsifying and gelling abilities (Li-chan, 1983). Complete solubility of WPC is necessary for optimum functionality in foams, emulsions, beverages and similar applications. Solubilities of spray dried WPC has been reported as 86.4, 93.32 have been reported for 26 and 45% protein levels (Jayaprakasha, 1992). Also the high degree of solubility of WPCs in acidic food products is one major advantage over casein products.
The emulsifying capacity is the amount of oil which can be emulsified by a certain amount of protein before a phase inversion occurred or the emulsion collapsed. The emulsion stability is the ability of a protein to form an emulsion which remains unchanged over a certain period of time under given conditions (Mulvihill and Fox, 1987). WPCs have a good emulsifying capacity, even better than non fat dry milk, which has proved useful to emulsifying the oils present in the food system. Lipids are generally considered to be detrimental to the functionality of WPCs, but they are able to improve the emulsifying ability (Modder and Jones, 1987). Foaming is the creation and stabilization of air bubbles in a liquid. Factors essential for formation of protein based foams are a rapid diffusion of proteins to the air water interface to reduce the surface tension. Whey protein which has not been denatured has good whipping and foaming properties. Physical properties such as solubility, dispersibility, wettability and sinkability affect the overall functional properties of WPCs. Jayaprakasha (1992) observed that with the increase in protein content, solubility and dispersibility slightly improved, where as , sinkability, wettability and bulk density slightly decreased.

WPCs contain sufficient residual lactose, lipids phospholipids and other prooxidants to render susceptible to lipid oxidation and Maillard browning reaction that result in development of aged and stale flavour (Morr and Foegeding, 1990). Lichten (1983) observed that when WPC powder having 35% protein was stored at 37°C and 75% RH, after 42 days of storage the soluble protein decreased by 14%. Changes in the functionality of dry WPC containing 52% protein during storage have been investigated by Hsu and Fennema (1989) and it was concluded by them that the storage temperature should not be higher than 20°C and water activity should not exceed 0.20. High water activities lead to protein insolubility and accelerated flavor
deterioration. Equilibrium relationship between moisture content of WPC and the water activity at any temperature thus need to be quantified in the form of moisture sorption isotherms.

2.6 Engineering Properties of Powdered Milk Products

Powdered milk products have been known in some parts of the world for several decades. Further there is a trend for newer powdered foods for their specific physico-chemical and functional characteristics. The properties of powder products are dependent on various factors, viz., equipment and processing conditions, heat-stability and pre-treatment of the concentrate, outlet air temperature and contact time, extent of pre-crystallization, agglomeration, etc. Engineering property data on powders with regard to its physical, functional and moisture sorption characteristics are required for heat and mass transfer evaluations in processing unit operations, product storage and its reconstitution. The bulk density of powders has pronounced influence on packaging costs. Free flowing properties, devoid of any stickiness and caking is an important commercial requirement of dried milk products for ease of handling. Powders are rehydrated before consumption. The structure, density and particle size play important role in reconstitution of powder in to milk. Reconstitutability of the product is the phenomenon of recombining milk powder with water and it includes the properties such as solubility, dispersibility, wettability and sinkability. Physical properties of a powder notably density, flowability and reconstitutability are determined by interrelationship between particle properties, such as, chemical composition, shape, size, porosity and surface roughness (Upadhyay, 2000). Powders are dynamic systems whose behaviour drastically changes in response to relatively minor modification of external storage conditions. The changes that occur in milk powder during storage are, to a large extent, dependent on the
processing conditions, the final composition of the powder and the storage conditions. The major physico-chemical and the functional properties of powders are discussed in this section, whereas the moisture sorption characteristics are presented in section 2.7.

2.6.1 Bulk density

Bulk density is a property of economical, commercial and functional importance. Also known as apparent or packing density, bulk density is regarded as mass of milk powder, which occupies a fixed volume and normally expressed in g/ml or g/cc. The total volume includes particle volume, inter-particle void volume and internal pore volume. Bulk density is not an intrinsic property of a material; it can change depending on how the material is handled. The producers are interested in high bulk density to reduce the shipping volume. In some cases the producer may be interested in low bulk density to supply apparently larger quantities of powder on the retail market than that of their competitors.

As per Fitzpatrick and Callaghan (1996) bulk density is a very complex property of milk powders and depends upon particle density, amount of interstitial air content, occluded air content and powder flowability. A high degree of whey protein denaturation has been reported to result in low occluded air content giving a high bulk density powder. Similarly, increase in feed solids also result in high bulk density, whereas increase in inlet air drying temperature and feed aeration decreases the bulk density.

Bulk density of powdered milk products have been reported by several research workers. Ilari (2002) has reported the loose and tapped specific weights of normal dried milk as 0.36 and 0.47 g/cm$^3$. According to Upadhyay (1989) the bulk density of normal spray dried cow milk powder may vary between 0.5 to 0.8 g/cc.
Patil (1980) has reported the loose and packed bulk density of soy-whey beverage powder as 0.42 and 0.69 g/cc, respectively. According to Jayaprakasha (1992), packed bulk density of spray dried whey powder varied from 0.51 to 0.58 g/cc. Jha et al. (2002) studied the physico-chemical properties of instant kheer mix powder. The freshly made kheer powder was reported to have a loose and packed bulk density of 0.65 and 0.81 g/cm³ respectively.

Buma (1972) reviewed the available literature on densities of milk constituents and found that the particle density of casein varied from 1.25 to 1.46 g/cm³. Munro (1980) studied the densities of various types of casein using gravimetric method. The reported values of lactic, sulphuric and rennet casein were 1.36, 1.37 to 1.40 and 1.44 to 1.47 g/cm³ respectively. Bhadania (1985) reported the bulk density of sun dried lactic acid casein from buffalo milk to vary between 0.444 and 0.541 g/cm³ and particle density as 1.352 g/cm³.

Boersen (1990) reported that high particle density contribute to high bulk density, improved reconstitution quality of powders in water, better shelf-life of fat-filled products like whole milk powder and reduction in stack losses of spray driers A two-stage spray drying system is reported to enable operation with high feed concentration and still keeping a low particle temperature distribution which is favourable for obtaining high bulk density (Pisecky, 1981). Bulk density of the powdered products is also affected by its storage. Bulk density of whey-mushroom soup powder is reported to decrease after storage at 37°C for 1 month (Ghosh, 1994). In a study on whey-kinnow juice powder Khamrui (2000) reported that the loose bulk density declined from 0.58 to 0.31 g/cc and packed bulk density declined from 0.85 to 0.30 g/cc, during storage at 45°C for 6 months.
3.6.2 Occluded and interstitial air contents

Buma (1971) explained that the presence of air in the atomized droplets causes occluded air in dried powder particles. The interstitial air in the powder is related to the bulk density of powder (Verhey and Lammers, 1973). The more the interstitial air in a powder, the lower its bulk density. The greater the degree of agglomeration, the more interstitial air is contained in the powder and the lower is the bulk density (Pisecky, 1985). The occluded air content of cow whole milk powder has been reported as 125 ml/kg by Hols and VanMill (1991).

2.6.3 Dispersibility

It reflects the ability of the wetted aggregates of powder particles to become uniformly dispersed when in contact with water. This property also helps in determining the instantness of a powder. It is related to the ease at which lumps and agglomeration fall apart. Large particle sizes of dried products are generally associated with good dispersibility (Buma, 1971). A high free fat content is usually considered unfavourable for better dispersibility of powders (Vilder et al., 1977). Dispersibility of whey-mushroom soup powder (Ghosh, 1994) and whey-kinnow juice powder (Khamrui, 2000) declined during storage, the decline being more pronounced at higher storage temperatures.

2.6.4 Wettability

The wettability of a powder is primarily a measure of its hydrophilic property, that is, the ability of the powder particles to be wetted by water. The tendency of powders to form lumps on adding water indicates lack of wettability. Wettability is measured as the time necessary for a given amount of powder to pass through the water surface under specified conditions. Wettability of whole milk powder is poor at
temperatures below the melting point of fat as particle surface is always covered by fat. The wettability of dry powder particles, generally, depends on the surface charge, particle size, density, porosity and the presence of amphiphilic substances (Lascelles and Baldwin, 1976; Sanderson, 1978; Jensen and Nielsen, 1982). For instant whey powders, wettability was observed to be 5 to 6 s (Jensen and Oxlund, 1988). Wettability of whey-based mushroom soup powder was reported to be 6.5 s (Ghosh, 1994). Wettability of powders has been found to decrease with storage. Whey-kinnow juice powder had excellent wettability, however, the wetting time increased from initial 18.3 to 36.1 s during storage at 45°C for 6 months (Khamrui, 2000). Wetting time of coffee complete powder increased, during storage for 3 months (Malhotra and Mann, 1989) and a similar increase in wetting time upon storage at 37°C for 3 months was reported for tea complete powder (Jha and Mann, 1996). Spray dried malted milk also suffered a decline in wettability during storage at 30°C for 2 months (Sanyal and Balachandran, 1989).

2.6.5 Flowability

The flow property of a powder refers to the ease with which powder will flow when a shearing force is applied. The flowability is one of the major functional properties of dried milk products, with considerable implications in packaging, metering into a process vessel, etc. (Patel, 1999). The flowability of powder is measured in terms of the angle of repose of a powder heap with the horizontal plane. The higher the angle of repose, the lower is the flowability. Cow skim milk powder has flowability from 44 to 45°, whole milk powder 65° and khoa powder 64.1° (Ranganadham, 1988). The angle of internal friction for skimmed milk powder was reported to vary between 36 and 44° (Ilari, 2002).
The flowability of Cheddar cheese whey powder and whey-based mushroom soup powder were reported as 32° and 58° by Jayaprakasha (1992) and Ghosh (1994), respectively. Jha et al. (2002) reported an angle of repose of 40.09° for instant kheer mix powder.

Long term storage of free flowing powders can result in flow problems due to a phenomenon known as time-consolidation, where a powder consolidates (solidifies) under its own weight over time. Studies on spray dried whey permeate powder demonstrated time-consolidation effects where its flowability was reduced with increasing time (Teunou, 2000). Increasing relative humidity and temperature of storage also resulted in a decreasing flowability of whey permeate powder (Teunou, 1999).

Ilari (2002) reported the flowability scale of powders from 0-19 very poor, 20-39 poor, 40-59 not good, 60-69 normal, 70-79 good, 80-89 fairly good and 90-100 very good. All the dairy powders have been close to the value of 60, corresponding to the “normal flowability”.

2.6.6 Insolubility index

Insolubility index is an indication of degree of denaturability and status of proteins as well as amount of scorched particles present in the powders, which vary with the severity of heat-treatments given during various processing steps. The insolubility index of various whey powders varied between 0.60 to 1.10 ml (Jayaprakasha, 1992). According to Indian Standard Institution, the maximum insolubility index of spray dried skim milk powder is 2.0 ml. Insolubility index of cow whole milk powder increased during storage period and increased more if the initial insolubility index was relatively high (Van Mil and Jans, 1991; Celestino et
Changes in insolubility index during storage was found to depend strongly on holding temperature, moisture content and heat-treatment of milk (Kudo et al., 1990).

Hsu and Fennema (1989) studied the functional properties of dry whey protein concentrate containing 52% protein at temperature ranging from -40 to 40°C and water activities ranging from 0.15 to 0.41. The solubility values of all samples varied from 73 to 92% during the study period. Of the storage variables studied the storage temperature and storage time were the most important and water activity was moderately important. It was suggested that to achieve good retention of the original attributes of the WPC during the storage period, the temperature should not be higher than 20°C and the water activity should not be higher than about 0.2.

Jha et al. (2002) investigated the physico-chemical properties of formulated instant kheer mix powder. The freshly made kheer powder was reported to have an insolubility index of 4.0 ml and wettability of 2 min.

Mistry and Pulgar (1996) reported the physical and storage properties of high milk protein powder (HMPP) prepared by ultrafiltration and diafiltration of skim milk to 21% protein and spray drying. The HMPP was reported to have lower loose and packed densities than non-fat dry milk but the true densities of both powders were similar. The solubility index rose in the HMPP when stored above 10°C but remained unchanged in non-fat dry milk.

Fitzpatrick (2004) studied the effect of powder properties and storage conditions on the flowability of milk powders with different fat contents and reported that whole milk powder is more cohesive than skim milk powder. Cohesion of milk powders increased with exposure to moisture in the air at 46% relative humidity and 20°C. The whole milk powder picked up less moisture than skim milk powder, due to
its high fat content. Consistent reliable flow of milk powders out of hoppers and silos is very important in their handling and processing.

Kim et al. (2005) investigated the effect of surface composition on the flowability of four industrial spray dried dairy powders, viz., skim milk powder, whole milk powder, cream powder and whey protein concentrate. The results obtained indicated that, although there are several parameters including particle size, which influence the flowability of powders, the flowability is strongly influenced by the surface composition of powders. It was found that skim milk powder flows well compared to other powders because the surface is made of lactose and protein with a small amount of fat, whereas the high surface fat composition inhibits the flow of whole milk, cream and whey protein concentrate powders.

2.7 Moisture Sorption Characteristics

2.7.1 Concept of water activity

Water activity is an important food preservation parameter. There are abundant qualitative observations that foods of high moisture content are readily subjected to deterioration by microorganisms (Scott, 1957). It has been realized that all the water present in a food is not available for microbial growth. Some of the water exists tightly bound to the product and hence cannot be utilized by the microbes. Thus, the state of water rather than the total content of water is important as far as microbial proliferation is concerned.

It has been observed that the state of water is related to the vapour pressure of a food. Greater the proportion of free water present, greater is the vapour pressure and vice-versa. Increased bound water reduces the vapour pressure. Thus, if a product is kept in a closed container and allowed to equilibrate, the humidity inside the container
will be a measure of free state of water inside the product. The distilled water shows a humidity of 100% and all foods show a humidity of less than 100%. For convenience, the humidity of food expressed in decimals is called as water activity of the food. The definition of water activity is a modified one of relative humidity (RH).

\[ a_w = \frac{v_p}{v_w} \]  

(2.1)

Where \( a_w \) is the water activity, \( v_p \) is the vapour pressure of a product and \( v_w \) is the vapour pressure of pure water.

The concept of \( a_w \) has opened up new vistas of research in food preservation. An in-depth research has been conducted with regard to microbial, chemical and textural relations of water activity. Several treatises have been published moisture sorption phenomenon and water relations in foods (Scot, 1957; Labuza, 1970; Rockland and Stewart, 1981; Simota and Multon, 1985; Rockland and Beuchat, 1987; Whittenbury et al., 1988; Bandyopadhyay (1987).

2.7.2 Sorption phenomenon

Generally foods when kept at different humidities adsorb or desorb moisture depending upon their water activity (Kapsalis, 1987). When \( a_w \) is less than the surrounding humidity, the product will adsorb moisture and when reverse is the case, it will desorb moisture. Therefore, when a product is equilibrated at different humidities, it will have different moisture contents. The product will have water activities corresponding to the humidities. The moisture content in the product on solid basis plotted on ordinate against the values of humidities on abscissa gives the sorption isotherm of that product. When the product with high moisture content is
kept at different humidities, it desorbs moisture and corresponding isotherm is called desorption isotherm, but when the same product is first dried and equilibrated at different humidities, it adsorbs moisture, the corresponding isotherm is known as adsorption isotherm.

The advantages of establishing isotherms of a product are: (i) water activity of a product can be obtained at any given moisture content, (ii) bound water, capillary water and multilayer water can be estimated and thermodynamic properties of product, such as enthalpy, Gibb’s free energy and heat of sorption can be computed. These aspects provide necessary insight into the sorption characteristics and drying phenomenon of a product (Kinsella and fox, 1987).

Sorption isotherms are usually classified according to their shape in five different types: I, II, III, IV, and V (Brunauer et al., 1940; Basu et al., 2006). Type I curves are convex upward throughout whereas Type III curves are concave upward throughout. Type II, IV, and V isotherms show one or more inflection points. Most food stuff including milk products generally show type II isotherm (Iglesias and Chirife, 1982).

Berlin et al. (1968) investigated the vapour sorption properties of spray dried whey, skim milk and whole milk powders. The initial sorption in the lower portion of isotherm was found to be much greater on milk powders than on whey powders. It was suggested that initial site of sorption in milk powder is not lactose glass, nor it is the whey proteins, but more likely water protein binding involving casein in the interaction. A break point was observed in the isotherms of milk powders in the water activity range of 0.52 to 0.625.
Lin et al. (2004) studied the desorption isotherms of whole and skim milk powders at elevated temperatures of 52.6, 69.4 and 89.6°C. The isotherm showed clear temperature dependence. The desorption isotherms of skim milk powder and whole milk powder were identical in the at temperatures of 53-90°C when the moisture content was calculated on a non fat basis. Inversion point in the isotherms was note that ranged from a water activity of 0.3 to 0.43 for skim milk powder and 0.28 to 0.40 for whole milk powder.

Sorption isotherms of several food products including proteins, lactose, whey powder, milk powder, cheese, yoghurt have been been established (Berlin, 1981; Saltmarch and Labuza, 1980; Wolf et al., 1973; Ruegg et al., 1985), but reports on indigenous dairy products are scarce, except those on peda, chhana powder and khoa (Biradar et al., 1985; Bandyopadhyay et al., 1987; Sawhney et al., 1988). There is no published work available on moisture sorption characteristics of dried milk products produced from buffalo milk.

2.7.3 Modeling sorption isotherm

The relation between moisture content and $a_w$ is not linear, but sigmoid which makes the prediction of $a_w$ from moisture content difficult. Various mathematical models have been proposed in literature to describe sorption isotherms. Some were developed with a theoretical basis to describe adsorption mechanism e.g. BET and GAB (Brunauer et al., 1940; Van den Berg and Bruin, 1981) whereas others are just empirical or a simplification of more elaborate models. In some ranges of water activity, sorption isotherm can be approximated to linear equations.

Chirife and Iglesias (1978) reported that models proposed by Halsey (1948) and Oswin (1946) are the most versatile two-parameter equations for describing the
sorption isotherms. **Caurie (1981)** developed a model which could help in evaluating properties of sorbed water. **Mizrahi and Karel (1977)** proposed a three parameter model that yielded a good fit for moisture sorption isotherms of several foods. In the COST 90 project on water activity, **Bizot (1983)** demonstrated that the ‘Guggenheim-Anderson-de Boer’ (GAB) equation was the three parameter theoretical model giving best fit for most food isotherms over a wide water activity range and also provides a better evaluation of the amount of water tightly bound by primary adsorption sites. **Singh and Singh (1996)** discussed the application of GAB model for water sorption isotherms of food products.

Dried food products usually show isotherms of Type II or III. It should be noted that in some cases these equations predict non-zero moisture content for zero water activity e.g. Chung Pfost equation (**Chung Pfost 1967**), Smith equation (**Smith, 1947**), Iglesias and Chirife equation 1 and 2 (**Iglesias and Chirife, 1982**), modified Chung Pfost equation (**Pfost et al., 1976**) Halsey equation (**Halsey, 1948**) and modified Halsey equation (**Iglesias and Chirife, 1976**). Some equations take into account the effect of temperature e.g. modified Chung Pfost equation, modified Henderson equation (**Thompson et al., 1968**) modified Halsey equation, Sowing equation (**Oswin, 1946**) and GAB equation. These models have been adopted as standard equations by the American society of Agricultural Engineers for describing sorption isotherms (**ASAE, 1995**). The equations of BET and GAB provide the monolayer moisture content and can be considered to be the most useful ones for determining optimum moisture content for good storage stability, especially for dehydrated foods (**Arslan and Togrul, 2006**).

**Stencl (1999)** studied the water activity of skimmed milk powder in the temperature range of 20-45°C. It was found that the water sorption capacity decreased
as the temperature increased. Of the four sorption models tested (Chung-Pfost, Halsey, Henderson and Oswin) to determine the best fit for the experimental data, the modified Oswin equation was found to be the best model for moisture adsorption and desorption of the skimmed milk powder. It was demonstrated that the increase in equilibrium moisture content was very small about 4% w.b. in the range of water activity 0.1 to 0.9. Higher levels of water activity than 0.9 resulted in a marked increase of equilibrium moisture content and susceptibility to spoilage by microorganisms. The hysteresis effect between moisture adsorption and desorption was found to be insignificant.

Kockel et al. (2002) reported the equilibrium moisture content of skim milk powder at elevated temperatures between 55-90°C and for relative humidities between 3.3 and 19%. It was reported that skim milk powder containing crystalline lactose showed moisture content of about only 605 of the skim milk powder with amorphous lactose suggesting that while the lactose in crystalline form is non hygroscopic sorptive behaviour of other components namely protein contribute solely to the hygroscopicity.

Foster et al. (2005) investigated the prediction of moisture sorption isotherms of dairy powders, namely, whey protein isolates, high miceller casein and milk protein concentrates powder. No temperature dependence was observed over the temperature range of 4-37°C, however at 50°C, the powders absorbed less moisture than observed at lower temperatures. The GAB isotherm model gave a good approximation of the isotherms over the temperature range of 4-37°C.

Iglesias and Chirife (1976a) evaluated the monolayer moisture content from literature data on moisture sorption isotherms of a large number of dehydrated foods and food components. The monolayer moisture content were found to decrease
significantly with increase in temperature and the observed effect was attributed to a reduction in the number of active sites as a result of physical and/or chemical changes induced by temperature. Monolayer moisture content was higher in desorption isotherm as compared to adsorption isotherm.

**Bhadania (1985)** developed desorption isotherms for hydrochloric acid industrial casein at 40, 50, 60 and 75°C. The parameters of Henderson equation were evaluated and the functional relationships between the constants and temperature were developed. The generalized model was found to predict the casein desorption behaviour satisfactorily.

**Bandyopadhyay (1987)** reported the moisture adsorption isotherms of lactose, casein skim milk and chhana powder at 50°C. The moisture sorption data was fitted to BET and Caurie’s equations. The casein adsorbs maximum amount of water at all water activities. A considerable amount of swelling was also observed in casein when it was incubated in the test chamber at relative humidities of 0.73. Local isotherms of the materials resulted on three intersecting straight lines with two points of discontinuity, which indicated the change in nature of water binding. The range of water activities at which the major changes took place were: casein 0.08 to 0.56, lactose 0.20 to 0.73, skim milk 0.12 to 0.72 and chhana powder 0.049 to 0.112. The monolayer moisture contents of casein, lactose and chhana powder as determined from BET equation were 4.9, 2.2 and 1.95% d.b. respectively. The same author reported the Caurie’s monolayer values as 6.3, 4.0 and 5.2% d.b. for respective milk products. Kinsella and Fox (1987) reported the values of estimated BET monolayer values for casein as 5.5%.

**Sawhney and Cheryan (1988)** established the moisture sorption isotherms of heat desiccated whole milk product khoa. The GAB model was found to be the best fit
model for describing the moisture sorption data of khoa. Monolayer moisture content of khoa was found to be 2.6169 g/100 g solids.

**Haque and Roos (2004)** investigated the water sorption and plasticization behaviour of spray dried lactose-protein mixtures. The mixture sorbed significantly higher amounts of water at relative vapour pressures below 32.15 and above 44.1%. At intermediate water vapour pressure between 33.2 and 44.1% pure lactose sorbed more water than lactose protein mixture. Both BET and GAB models were applicable for the prediction of water sorption over the experimental water vapour pressure ranges.

**Stencel (2004)** investigated the modeling of water sorption isotherm of yoghurt powder spray on the equilibrium data for adsorption and desorption in the temperature range of 20-40°C. Four sorption models Chung-Pfost, Halsey, Henderson and Oswin were tested to determine the best fit for the experimental data, the modified Chung-Pfost equation was found to be the best model for moisture adsorption and desorption of the skimmed milk powder. The critical value of equilibrium moisture content of the sample tested, corresponding to water activity 0.6, was 8.1-8.6 w.b. at 20°C.

**Jayaraj et al. (2006)** investigated the moisture sorption characteristics of *chhana podo* at 5 and 35°C. Amongst the 12 sorption models tested, the Caurie’s model was found to be the best to describe the isotherm. As the temperature of sorption increased from 5 and 35°C, a reduction in moisture sorption and water binding capacity was observed. The percent bound water, density of sorbed water, number of adsorbed monolayers and surface area of adsorbent decreased with increase in temperature.

**Menkov and Durakov (2007)** reported the moisture sorption isotherms of sesame flour at 10, 25 and 45°C. Of the five sorption models tested (modified Chung-
Pfost, modified Halsey, modified Henderson, modified Sowing and GAB) to determine the best fit for the experimental data, the GAB model was found to be most suitable for describing sorption data. The BET equation was used to evaluate the monolayer moisture content.

**Ko (2008)** reported the moisture sorption isotherms of domestic and imported milk powders and their calculated heat of sorption. Monolayer moisture content was evaluated using BET equation and was found to vary between 3.53 and 5.07 g/100g solids at 15 °C, it decreased with increase in temperature. Heat of sorption as calculated using Clausius-Clapeyron equation was found to be 18.23 kJ/mol at 5% moisture content, it decreased to 1.50 kJ/mol at 30% moisture content.

**Sahu and Jha (2008)** studied the adsorption isotherm of sandesh, one of the popular Indian milk sweet, at 20 and 30°C. Out of the three sorption models BET, Caurie and GAB fitted to the experimental data, Caurie model was found to be superior in interpreting the moisture adsorption characteristics of sandesh. The density of sorbed water and surface area of adsorbent at 20°C as calculated from Caurie model was found to be 2.204 g/cm³ and 72.774 m²/g respectively. The effect of increase in temperature from 20 to 30°C was to decrease the density of sorbed water and surface area of adsorbent.

For milk products, the Halsey equation is reported to give best description of the experimental data followed by Mizrahi equation that gives fair representation of dairy products (**Boquet et al., 1978**). Using BET equation, **Heldman et al. (1965)** calculated monolayer moisture content of high heat, medium heat and low heat non-fat dry milk at 16°C as 11.34, 10.00 and 9.30% d.b. respectively. **Berlin et al. (1973)** reported bound, unfreezable water content in whey powders 4.5 to 5.2 g per 100g protein. For caseins subjected to different heat treatments, the monolayer water content as estimated from BET equation ranged from 5.06 to 6.16 g per 100 g (**Ruegg et al., 1979**).
2.7.4 Temperature dependence of sorption phenomenon

The knowledge of temperature dependence of sorption phenomenon provides useful information on the energetics of water sorption process in foods (Rizvi, 1995). The net isosteric heat is useful in estimating the state of adsorbed water by solid particles, which is a measure of the physical, chemical and microbial stability of food in storage (Labuza, 1968).

The monolayer moisture content depends on the temperature at which the isotherm was established. In general, monolayer values decrease with increasing temperature of equilibration. This may reflect structural difference with fewer polar site being available at higher temperatures. Weisser (1985) proposed using the exponential relationship between GAB parameters ($W_m$, $C$, and $k$) and temperature to extend the GAB model to incorporate the temperature effect. The temperature dependence of isotherm parameters was thus determined by correlating the GAB (T) constants with temperature by using the following form of Arrhenius-type of equations:

\[
C(T) = C' \exp \left( \frac{H_1 - H_m}{RT} \right) \tag{2.2}
\]

\[
k(T) = k' \exp \left( \frac{H_L - H_m}{RT} \right) \tag{2.3}
\]

\[
W_m(T) = W'_m \exp \left( \frac{\Delta H'}{RT} \right) \tag{2.4}
\]

Where:

\[H_1 = \text{total heat of sorption of the first layer on primary sites}\]

\[H_m = \text{total heat of sorption of the multilayer which differs from the heat of condensation of pure liquid water}\]

\[H_L = \text{heat of condensation of pure water vapour}\]

\[\Delta H' = \text{the partial molar enthalpy of sorption}\]

\[R = \text{the universal gas constant, J/(mol-K)}\]
Sawhney et al., (1991) studied the effect of temperature on moisture sorption isotherms of khoa. In the temperature range 15-45 °C. The equation describing the temperature dependence of GAB constants were determined in the form of Clausius – Clapeyron equation by which equilibrium moisture content could be calculated for any given water activity at any temperature. The net isosteric heat of desorption of khoa was found to decrease from 19.5 kJ/mol at moisture content of 0.05 g/g solids to 0.43 kJ/mol at moisture content of 0.25 g/g solids.

Arogba (2001) reported the effect of temperature on moisture sorption isotherm of biscuit containing processed mango kernel flour. Equilibrium moisture content increased with decrease in storage temperature at any water activity. The Henderson equation predicted the isotherm better than BET. The calculated monolayer moisture content using the BET equation was found to be independent of storage temperature.

Jayendra et al. (2005) studied the effect of temperature on the moisture desorption isotherm of kheer in the temperature range of 10-40°C. There was in general a negative temperature effect on equilibrium moisture content at low water activities but curves at 25 and 40°C showed inversion above water activity of 0.6. The GAB sorption model gave the best fit to desorption data at all temperatures. Monolayer moisture obtained from both BET and GAB equations were not significantly different and decreased with increase in temperature.

2.7.5 Thermodynamic aspects of water sorption

Changes in thermodynamic properties such as enthalpy, entropy, free energy of sorption of water upon binding to proteins under equilibrium conditions may aid in studying the nature of binding. When water is adsorbed on to a protein, heat is evolved as new bonds are established (Kinsella and Fox, 1987). Hence, sorption
isotherms determined at different temperatures can be used to estimate the strength of binding and elucidate other thermodynamic phenomenon (Iglesias and Chirife, 1982).

The isosteric heat of sorption or differential enthalpy is an indicator of the state of water absorbed by the solid material. The net isosteric heat of sorption (\( \Delta h_d \)) is the amount of energy by which the heat of vaporization of moisture in a product exceeds the latent heat of pure water (\( \Delta H_d \)) (Tsami, 1991). The net isosteric heat of sorption is calculated from the experimental sorption data by linearization of the following form of Clausius-Clapeyron equation applied to two temperatures (Weisser 1985).

\[
\left[ \frac{d(\ln a_w)}{d\left(\frac{1}{T}\right)} \right]_w = \frac{\Delta h_d}{R} \tag{2.5a}
\]

\[
\ln \left( \frac{a_{w1}}{a_{w2}} \right) _w = \frac{\Delta h_d}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \tag{2.5b}
\]

And

\[ \Delta H_d = \Delta h_d + \Delta H_{vap} \tag{2.6} \]

The ‘\( \Delta h_d \)’ is a differential quantity, the value of which corresponds to sorbed molecules at a particular moisture content ‘\( w \)’. Plotting the experimental sorption isotherm in the form ‘\( \ln a_w \)’ versus ‘\( 1/T \)’ at more than two temperatures for a specific moisture content, ‘\( \Delta h_d \)’ was obtained from the slope (-\( \Delta h_d / R \)). This procedure is based on the assumption that ‘\( \Delta h_d \)’ is invariant with temperature and requires measurement of sorption isotherm at more than two temperatures. The differential enthalpy (\( \Delta H_d \)) is obtained by adding the enthalpy of vaporization of water at the given temperature to the net integral enthalpy.

Rizvi (1995) explained that the differential entropy (\( \Delta S \)) of adsorption and desorption of water at each moisture content could be obtained from the relationship of differential enthalpy and Gibb’s free energy

\[ \Delta S_v = \frac{\Delta H_d - \Delta G}{T} \tag{2.7} \]
Thermodynamic calculations based on Clausius-Clapeyron equation have been used to establish the enthalpies of sorption and desorption. In general, the enthalpy decreases as the water activity increases. Differential enthalpy of protein has been found to decrease as moisture content increased from 0.05 to 0.3 g water per 100 g protein (Kuntz and Kauzman 1974).

Al-Muhtaseb (2004) investigated the moisture sorption isotherms and thermodynamics characteristics of starch powders. It was reported that Clausius-Clapeyron equation facilitated satisfactorily the determination of isosteric heat of sorption. An exponent relation was found to adequately describe the dependence of net isosteric heat of sorption on equilibrium moisture content. The net integral entropy increased decreased with increasing moisture content, while net integral entropy increased continually with water content.

Togrul and Arslan (2007) reported that isosteric heat in walnut kernels decreased with increase in moisture content and approached the latent heat of pure water. As the moisture content increased, the difference in isosteric heat values for adsorption and desorption processes were observed to decrease. Adsorption entropy increased with increasing moisture content up to 2.5% d.b. and then decreased sharply with further increase in moisture content.

Kane et al. (2008) studied the moisture sorption isotherms and thermodynamic properties of tow mint at 30, 40 and 50°C. Modified Halsey, GAB and Peleg were found to satisfactorily fit the sorption data. The differential enthalpy and entropy decreased with increasing moisture content and were adequately characterized by power law equation.
McMinn and Magee (2003) studied the thermodynamic properties of moisture sorption of potato and reported that the GAB and Halsey models were found to adequately describe the sorption characteristics. Isosteric heats (differential enthalpies) were calculated through direct use of moisture isotherm by applying the Clausius-Clapeyron equation. At a specific moisture content, the isosteric heat of desorption is higher than the corresponding adsorption value. This was explained in terms of increased energy requirements of former process which is indicative of more polar sites on the surface of the material. As the moisture content increased the difference in heat values of two processes was observed to decrease. The net integral entropy of adsorption and desorption were observed to decrease with moisture content. Minimum entropy values of -60.0 kJ mol\(^{-1}\) K\(^{-1}\) for adsorption and -29.8 kJ mol\(^{-1}\) K\(^{-1}\) for desorption at moisture content of 0.068 and 0.053 kg/kg.

Water binding energy of a food varies with the nature of the food as well as the state of water in it. Soekarto and Steinberg (1981) stated that binding energy for each fraction of water in a food is constant and the total energy balance represents composite binding energy. For soy flour, they reported values of -1083, +265 and -73 cal/mole for primary, secondary and tertiary water states.

**2.7.6 Moisture sorption hysteresis**

Water sorption hysteresis is the phenomenon according to which two different path exist between the adsorption and desorption isotherms. Desorption isotherm usually lies above the adsorption isotherm forming a closed hysteresis loop. Moisture sorption hysteresis has important theoretical and practical implications in foods. Due to hysteresis, a much lower vapour pressure is required to reach a certain amount of water by desorption than adsorption. (Kapsalis, 1987). Interestingly, Acott and Labuza (1975) had shown that a few fungi and bacteria grew rapidly in system prepared by desorption process than by adsorption at the same water activity.
A variety of hysteresis loop shapes can be observed in foods. In high protein foods, a moderate hysteresis begins at high water activity in capillary condensation region and extends over the rest of isotherm to zero $a_w$ and both adsorption and desorption isotherms are sigmoid in shape. (Kapsalis, 1981). High molecular weight polymers, such as proteins may immobilize large quantities of water as gels and show marked hysteresis explained in terms of capillary condensation theories and steric arrangements (Aguilera and Stanely, 1999). It has been known that sorption hysteresis is affected by temperature and properties of components. In general the effect of increasing temperature was to decrease the total hysteresis as well as to limit the span of loop along the isotherm. However, in some foods like ginger and nutmeg the total hysteresis remained constant or increased in spices like cinnamon and coriander.

Moisture sorption hysteresis has been related to the nature and state of components of foods and temperature (Zhengyong et al., 2008). Hysteresis in foods is mainly because of their porous nature. Four theories have been put forward in order to explain hysteresis phenomenon based on porous nature of foods, namely, incomplete wetting theory, ink bottle neck theory, open pore theory and domain theory. Hysteresis in biopolymers is generally attributed to a deformation of the polypeptide chains within the protein molecule as the polar adsorbates occupy suitable positions for hydrogen binding or dipole interaction (Kapsalis, 1987).

Sawhney et al. (1996) evaluated the water vapour sorption hysteresis in khoa at 25 and 45°C. Hysteresis effect was found to be moderate in the monolayer moisture content region, it occurred predominantly in the water activity range 0.35 to 0.80 and then decreased at higher water activities. Hysteresis loop was classified as Type-C according to Everett classification. The effect of temperature was to decrease the hysteresis.
Al-Muhtaseb (2003) reported that hysteresis is evident over entire range of water activities in potato starch powders and empirical four parameter Peleg model and kinetic three parameter GAB model were found to best represent sorption experimental data.

2.7.7 Moisture sorption and surface area

Water sorption is influenced by surface area, composition, the number of surface binding sites and the porosity of protein particles. The number and size of pores in protein matrix determine total sorption area and the size and surface properties of pores influence rate and extent of hydration. The surface of foods possesses a high energy. As water is adsorbed, changes occur especially around the BET monolayer, where the surface area rapidly decreases (Berlin, 1981). This may reflect conformational changes in the macromolecules of casein (Kinsella and Fox, 1987). The surface area is generally calculated by equations given by Heldman et al., (1965) and Caurie (1981). Heldman et al. (1965) reported values of 238 to 354 m$^2$/g for various milk powders. As high a value of 1200 for casein and 800 for cheese were reported by Geurts et al., (1974). It has been noticed that marked disparities exist in published data on surface area of proteins. Igbeka and Blaisdall (1982) calculated the pore size distribution in Bologna meat product, which ranged from 2.6 to 27.7 Å, depending upon water activity; the pore size increased with increasing water activity and temperature of measurement.