

## CHAPTER II

### LITERATURE REVIEW

#### A. TAMARIND

Tamarind has been cultivated in India for centuries and now is widely grown in the topical countries. The name tamarindus come from the Arabic *Tamar-hindi*, meaning 'date of India', and refer to as the date like pulp inside the pods (Williamson, 2002).

1. **Botanical name** : *Tamarindus indica* Linn.

2. **Family** : Ceasalpiniaceae

3. **Common names** : Tamarind, Makhaam

4. **Local name** : Ta luup (Chaobon-Nakhon Ratchasima), Mong khlong (Karen-Kanchanaburi), Mot-le, Saa-mo-kle (Karen-Mae Hong Son), Maak kaeng (Shan-Mae Hong son), Am-pain (Khmer-Surin), (Fransworth and Bunyaphrathasara, 1992). In the other countries used to call each other such as Persians and the Arabs called it "tamar hindi", Malaysian called "Asam Java", Indonesian called "Asam", Burma called "Magyee" (วิถีนารท พันธุ์วุฒิ, 2545).

#### 5. Habitat

The tree is native to tropical Africa and is now naturalized and widely cultivated throughout India as well as other tropical countries, including the Caribbean, south east Asia and China, where is found on roadsides and in garden. (Williamson, 2002) Tamarind have 2 species in Thailand, there are sweet tamarind and sour tamarind. Most tamarind growing province are Loei, Phetchabun and Nakhonratchasima. The tamarind is the provincial tree of the Phetchabun province of Thailand (วิถีนารท พันธุ์วุฒิ, 2545)

## 6. Botanical description

*Tamarindus indica* Linn. is large tree, up to 30 m. high, having spreading branches. The bark is brownish-gray, peeling of in flaked. Leaves are even-pinnate, consisting of 10-18 pairs of small leaflets, rather closed together, petioles and rachis 5-12 cm long; leaflets oblong, 8-30 by 3-9 mm, opposite, pink or reddish when young, membranous, glabrous, apex obtuse or rounded, base unequal (Figure 1).

In florescence is in terminal raceme, yellowish-orange or pale green; consisting of calyx-tube narrow turbinate, with 4 imbricate segments, 1 cm long; petals 3, unequal, upper cordate, about 1 cm long, 2 lateral ones, narrowed towards the base; fertile stamens 3, base connate; ovary linear, about 7 mm long, pubescent, on a stalk adnate to calyx-tube. Pods are oblong, slightly curved, 5-15 by 1-2.5 cm, reddish brown. Seed is glossy, dark brown, embedded in a thick, sticky aromatic and acid brown pulp (Farnsworth and Bunyaphatsara, 1992; Williamson, 2002).

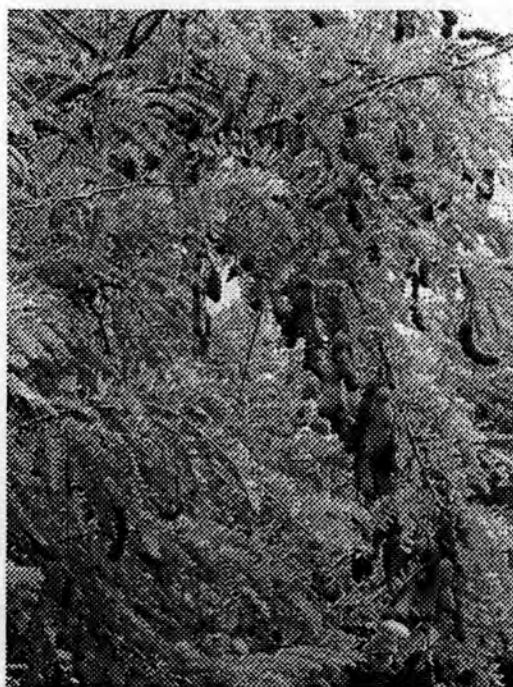


Figure 1 Tamarind tree

### **7. Parts used**

Many parts of tamarind are useful. They are fruits, fruit pulp, seeds, leaves, flowers and bark have long been used in traditional medicine (Williamson, 2002).

### **8. Ethanomedical use**

In Thai traditional text books, efficacies of tamarind are claim as follows: (Farnsworth and Bunyapraphatsara, 1992).

- Roots: Root of tamarind is used for wound healing and treatment of herpes simplex infection as an astringent.
- Bark: bark of tamarind is used as astringent for wound healing, treatment of herpes simplex infection, external ulcers abscesses and diseases in oral cavity.
- Pith: pith is used for pacification of blood circulation, treatment of menstrual disorder, pyometra and venereal diseases.
- Leaves: leaf of tamarind is used for improvement of menstrual blood quality, treatment for coughs, common cold, conjunctivitis and dimness vision, as a diaphoretic, antidysenteric, laxative, carminative and expectorant. Moreover, leaf is used as a gargle for aphthous ulcers and sore throats and for washing indolent ulcers.
- Fruit pulp: tamarind pulp use for improvement of menstrual blood quality, treatment of cough, severe disorders of three origins occurring during exposure to open fire after giving birth, abscesses, insect bite, fever, bleeding from the vagina, as an laxative, expectorant, enema, carminative and blood tonic.

- Unripe pod: unripe pod is used for improvement of menstrual blood quality, as an antiobesity, laxative and antipyretic.
  
- Seed: tamarind seed use for anthelmintic, antidiarrheal, emetic and tonic.
  
- Seed coat: Seed coat of tamarind seed is used for wound healing, treatment of wound, burns and wounds in diabetic patients, as antioxidant and antidysenteric.

In other parts of the world the plant is equally regarded: in Nigeria, leaf extract are used in guinea worm infection; in Fiji, the fruit and leaves are taken orally for pills and in Tanzania, a decoction of dried leaves is given for malaria. In Guatemala the dried fruit is taken as a febrifuge, for urinary tract infections and infections of the skin and mucosa, including ringworm and other fungal diseases. The bark is used as a tonic and febrifuge and the ash obtained by heating it with salt in an earthen pot is mixed with water and taken orally for colic and as a gargle or mouth wash. In the Canary Islands the dried fruit is eaten as a choloretic. Tamarind seed xyloglucan is use as a thickener, stabilizer, gelling agent and starch modifier for food, textile and toiletry use (Williamson, 2002).

#### **9. Ethnoveterinary usage**

The bark is used to treat intestinal parasites in swine. Fruits and leaves are given to ruminant for fever, intestinal parasites, bloat and as an appetizer, to pigs for coughs and colds, and to both for constipation. The leaves have been used to treat fractures (Williamson, 2002).

#### **10. Major chemical constituents**

Many chemical compounds were found in many part of tamarind. They were describing as follow this (Williamson, 2002).

### **10.1 Cardenolides and bufodienolides**

Uzarienin-3-O- $\beta$ -D-xylopyranosyl- $\alpha$ -L-rhamnopyranoside and scilliphaeosidin 3-O- $\beta$ -D-glucopyranosyl-L-rhamnopyranoside have been isolate from the seed.

### **10.2 Phytosterols and trierpenes**

Seed of tamarind have phytosterols and trierpenes. They are  $\beta$ -silital, campesterol, stigmasterol and  $\beta$ -amyrin.

### **10.3 Polysaccharides and sugars**

Many palyaccharides and sugars were found, they are arabinose, ribose, xylose, mannose, fructose, galactose, glucose, inosital, sucrose, maltose, raffinose, xyloglucan and polyose (a polysaccharide gum) are present in the seed. Pectin, glucose, mannose, maltose and arabinose are in the fruit.

### **10.4 Flavones and flavonols**

Flavones and flavonols are occur in leaf. They are apigenin, vitexin, isovitexin, orientin and others.

### **10.5 Oraganic and amino acids**

Aspartic, glutamic, tartaric, citric, oxalic and succinic acids, serine, methionine, phenylalanine and others are present in the fruit and seeds and glyoxalic, oxaloacetic, oxalosuccinic and  $\alpha$ -oxoglutaric acid in the leaf and seed.

### **10.6 Vitamin**

Vitamins in fruit are L-ascorbic acid, tocopherol, and carotenes.

### **10.7 Minerals**

Mineral in fruit are calcium, phosphorus, magnesium, potassium, sodium, copper, iron, zinc and manganese.

### 10.8 Fatty acids

Fatty acids are present in the seed of tamarind. They are palmitic, oleic acid, linoleic, arachidic, behenic, lignoceric, linolenic and decosatetraenoic acid.

### 10.9 Monoterpenoids and other volatile

Fruit of tamarind consist of 2-acetyl furan, benzaldehyde, phenyl acetaldehyde, dibutyl phthalate, furfural, linalool, linalool oxides, geraniol,  $\alpha$ -terpineol, tamarindineal (5-hydroxy-2-oxo-hexa-3,5-dienal) and others.

## B. TAMARIND PULP

Tamarind is the economic plant. They gave amount of tamarind pulp for a year. Tamarind is available in specialty food stores worldwide in pod form, tamarind paste or concentrate. Further more they were export to many countries.



Figure 2 Fruits of tamarind

### 1. Description

The fruit of tamarind are about 5-15 cm long. They have a brittle epicarp, pulpy mesocarp, through which run from the stalk about five to nine branched fibers,

and leathery endocarp. The latter forms from four to twelve chambers, in each of which is a single seed (Figure 2) (Evans, 2002).

Tamarind pulp appear reddish-brown color, moist and sticky mess in which yellow-brown fibers, pleasant and fruity odor, sweet and acid taste.

## 2. Chemical compositions

Pulp of tamarind contain many composition chemistry. There are reducing sugar (25-40 percent), organic acid (8-18 percent tartaric acid, 2 percent of other organic acids are present, malic and citric acid) 2-3.5 percent pectin, 2-3 percent proteins, fiber and cellulosic material. Almost of tartaric is combined from, chiefly as potassium bitartrate and calcium tartrate. (Lewis and Neelakantan, 1964; Grieve, 1975; Kapoor, 2001; Evans, 2002; Wiart, 2002) The tartaric acid is in dextrorotatory form. It synthesized from actively metabolizing leaves of this plant and then translocated to storage in fruits as their development. Sugar manufactured from pulp and act as a preservative (Lewis and Neelakantan, 1964; Evans, 2002).

Organic acids were found in tamarind pulp. Structure of tartaric and other organic acid in tamarind pulp are alpha-hydroxy acid or as show in Figure 3-5. Properties of chemical compound in tamarind pulp are described below.

### 2.1 Tartaric acid

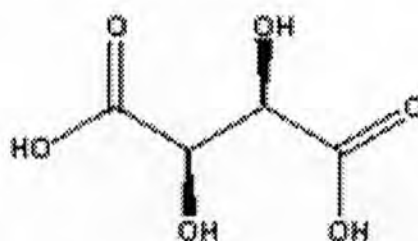


Figure 3 Structure of tartaric acid

L-tartaric acid (dextrotartaric acid) are natural tartaric acid. It is widely distributed in nature, classified as fruit acid. It occurs in many fruits, free and

combined with potassium, calcium or magnesium. Tartaric acid has monoclinic sphenoidal prism, melting point (mp) in range 168-170°C. Tartaric acid is stable to air and light. It has strong acid taste. It is strong organic acid. Chemical structure of tartaric acid dicarboxylic acid is shown in Figure 3. It has two  $pK_a$ ;  $pK_{a1}$  2.98 and  $pK_{a2}$  4.34. It is freely soluble in water.

## 2.2 Malic acid

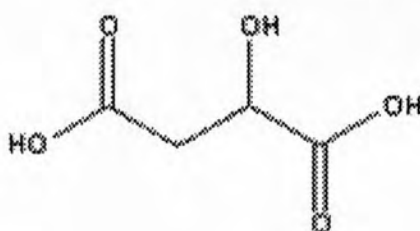


Figure 4 Structure of malic acid

Malic acid, the naturally occurring isomer is the L-form, has been found in apples and many other fruits and plants. Solubility of malic acid in water is 36.35 g/100 g. It is dicarboxylic acid, chemical structure is shown in Figure 4, it has two  $pK_a$ ;  $pK_{a1}$  3.4 and  $pK_{a2}$  5.13.

## 2.3 Citric acid

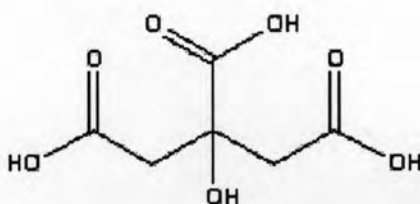


Figure 5 Structure of citric acid

Citric acid is widely distributed in plants and in animal tissues and fluids. It is soluble in water. Chemical structure of citric acid is tricarboxylic acid,



chemical structure is shown in Figure 5 it has three  $pK_a$ ,  $pK_{a1}$  3.128,  $pK_{a2}$  4.761 and  $pK_{a3}$  6.396.

### 3. Use

Pulp is an important ingredient of Indian and Thai cuisine. Fresh fruit are eaten and made into refreshing drink and jams. The ripened fruit is sweeter, yet still distinctively sour, and can be used in desserts and sweetened drinks, or as a snack. (Evans, 2002) In Thailand, there is a carefully cultivated sweet variety with little to no tartness grown specifically to be eaten as a fresh fruit. Overripe fruit pulp used to clean silver, copper and brass shrine furniture, removing dulling and the greenish patina that forms. In traditional cosmetic use, tamarind pulp is used as scrub for lightening skin.

### 4. Stability

Unlike in other fruits, ripe tamarind is not decreased in acid content. The formation and breakdown of starch in a short period during process of ripening results in 25-40 percent of reducing sugars, and give it sweet and sour taste. During storage, reddish-brown pulp becomes darker and after about a year it is almost black, that occurs due to Maillard reaction, since free amino acids and reducing sugar are presented in the fruit (Lewis and Neelakantan, 1964).

## C. SKIN COLOR

The color of the skin and hair is primarily due to the existence of pigment bodies known as melanin. Melanin is produced in the melanosome, membrane-bound organelles that are transferred to keratinocytes, probably by a process involving phagocytosis, to provide a uniform distribution of pigmentation. Visible pigmentation is depended on the amount, shape and size of melanosome, and chemical nature of melanin.

Melanin may be produced in either pheomelanins (yellow/red) or eumelanins (black/brown) color. The resulting pigmentation is finally cleared by degradation of melanin during the ascent of keratinocytes towards the outer stratum corneum. The remaining melanin pigments are shed with desquamation. If the melanocyte density and distribution are altered, disorders of pigmentation are appearing. One example is given by the typical pigmentary changes appearing during intrinsic ageing and photoageing. Melanin production is increased by exposure to the sun and plays a role in protecting the skin from sunlight. Ultraviolet radiation appears to increase production of precursor hormone proopiomelanocortin, which increases  $\alpha$ -MSH production, resulting in increased level of eumelanins (Schmitt, 1996; Petit and Pierard, 2003; Rabe et al., 2006).

#### **D. SKIN LIGHTENING AGENT**

Skin lightening agents are commonly available as shown in Table 1. In cosmetic formulation they contain one or several different active compounds. They may correspond to prescription drugs, over-the-counter products and cosmetics. There are indeed major differences in product registration requirements in various countries and markets.

Given the considerations, the skin lightening agents can be classified following the mechanism of melanogenesis inhibition. However, some agents act several steps of the process. In addition, most of the proprietary skin lightening formulations contain a combination of compounds in order to provide better efficacy by supplementary or synergistic action (Petit and Pierard, 2003).

Table 1 Classification of depigmenting agents (Briganti et al., 2003).

<b>Before melanin synthesis</b>	
Tyrosinase transcription	
C <sub>2</sub> -ceramide	Tretinoin
Tyrosinase glycosylation	
Calcium D-pantetheine-S-sulphonate	
<b>During melanin synthesis</b>	
Tyrosinase inhibition	
Hydroquinone	Kojic acid
4-hydroxy-anisole	Methyl Gentisate
4-S-cystaminyphenol	Ellagic acid
Arbutin	Resveratrol
Aloesin	Oxyresveratol
Azelaic acid	
Peroxidase inhibition	
Methimazole	Phenol/Catechols
Product reduction and ROS scavengers	
Ascorbic acid	$\alpha$ -Tocopherol
Ascorbic acid plamitate	D,L- $\alpha$ Tocopherol ferulate
Magnesium-L-ascobyl-2-phosphate	Hydrocumarins
Thioctic acid	
<b>After melanin synthesis</b>	
Tyrosinase degradation	
Linoleic acid	$\alpha$ -Linolenic acid
Inhibition of melanosome transfer	
Serine protease inhibitors	Niacinamide
Lecthins and Neoglycoproteins	RW-50353
Soybean/milk extract	
Skin turnover accerleration	
Lactic acid	Retinoic acid
Glycolic acid	Linoleic acid
Liquiritin	

## **E. SPRAY DRY**

### **1. Spray-drying process**

Spray-drying is a drying process which is widely used in large scale production. Spray drying consists of 4 processes as following (Masters, 1979).

- (1) Atomization of feed into a spray
- (2) Spray-air contact (mixing and flow)
- (3) Drying of spray (moisture/volatiles evaporation)
- (4) Separation of dried product from the air

Each stage is carried out according to dryer design and operation, and, together with the physical and chemical properties of the feed, determines the characteristics of the dried product. The spray homogeneity following atomization and the high rates of moisture evaporation (spray-air mixing and flow) enable the temperature of the dry product to be considerably lower than the drying air leaving the drying chamber. The product is thus not subjected to high temperatures, and when separate from the drying air is devoid of any heat degradation.

#### **1.1 Atomization of feed into spray**

The formation of spray (atomization) and the contacting of the spray with air are the characteristic features of spray drying. The selection and operation of the atomizer is of supreme importance in achieving economic production of top quality products. The atomization stage must create a spray for optimum evaporation conditions leading to a dried product of required characteristics.

Rotary atomizers and nozzles are used to form sprays. With rotary atomizer centrifugal energy is utilized. There are two categories of rotary atomizers: (a) atomizer wheels, (b) atomizer discs. Wheel designs are available to handle feed rates up to 200 t/h. With nozzle atomization, pressure, kinetic or (less common) sonic energy is utilized. There is a wide range of nozzle sizes and designs to meet spray-

drying needs. Feed capacities per nozzle are lower than per rotary atomizer, leading to nozzle duplication to meet high feed rate requirement.

### **1.2 Spray-air contact (mixing and flow)**

The manner in which spray contacts the drying air is an important factor in spray dryer design, as this has great bearing on dried product properties by influencing droplet behavior during drying. Spray-air contact is determined by the position of the atomizer in relation to the drying air inlet. Many positions are available. The spray can be directed into hot air entering the dryer chamber. Product and air pass through the drier in 'co-current' flow, i.e. they pass through the dryer in the same direction. This arrangement is widely used, especially if heat-sensitive products are involved. Spray evaporation is rapid, the drier air cools accordingly, and evaporation times are short. The product is not subject to heat degradation.

Alternatively, the spray can be contacted with air in 'counter-current' flow. Spray and air enter at the opposite ends of the dryer. This arrangement offers dryer performance with excellent heat utilization, but it does subject the driest powder to the hottest air stream. It readily meets granular powder requirements of non-heat-sensitive products.

### **1.3 Drying of spray (moisture/volatiles evaporation)**

As soon as roles of the spray come into contact with the drying air, evaporation takes place from the saturated vapor film which is quickly established at the droplet surface. The temperature at the droplet surface approximates to the wet bulb temperature of the drying air. Evaporation takes place in two stages. At first there is sufficient moisture within the droplet to replenish that lost at the surface. Diffusion of moisture from within the droplet maintains saturated surface conditions and as long as this lasts, evaporation takes place at a constant rate period or first period of drying. When moisture content become too low to maintain saturated conditions, the so-called critical point is reached and a dried shell forms at the droplet surface.

Evaporation is now dependent upon the rate of moisture diffusion through the dried surface shell. The thickness of the dried shell increased with time, causing a decrease in the rate of evaporation. This is termed the falling rate period or second period of drying.

#### **1.4 Separation of dried product from the air**

Product separation from the drying air follows completion of the drying stage, when the dried product remains suspended in the air. Two systems are used to recover the product.

System 1: primary separation of dried product takes place at the base of the drying chamber. During operation, the majority of product falls to the base of chamber, while a small fraction passes out entrained in the air and is recovered in the separation equipment. Such equipment is usually cyclones as the dry collector followed by wet scrubbers as the final wet collector. Alternative dry collectors are bag filters and electrostatic precipitators.

System 2: total recovery of dried product takes place in the separation equipment. This system places great importance on the separation efficiency of the equipment, but the system is often utilized, as it does not need a product-conveying system.

## **2. Advantage and disadvantage of spray drying technique**

The spray drying technique has several advantages in drying technique, as follow (Masters, 1979; Benita, 1996; Madene et al., 2006).

- (a) The majority advantage of spray drying can be used with heat sensitive products.
- (b) Equipments are available.
- (c) The spray drying technique uses low process cost, cost effective.
- (d) Carrier solid are widely used in this process.

- (e) Finished products are good stability.
- (f) Spray drying technique is continuous processing, suitable for use in large scale production.
- (g) Drying process is only one step and rapidly to process.
- (h) Process is flexibility method, difference encapsulation polymers, processing parameter can be used in the spray drying in order to perfectly adapt to the product requirement.
- (i) Spray drying technique is easy Good Manufacturing Practice (GMP) scaling up.

However, the spray-drying process has the limitation and the disadvantages, which should be considered. Spray-drying process preferred water as solvent. Carrier should be soluble or dispersible in water. It is importance to stress that low boiling point compounds with a finite degree of water solubility have posed a persistent problem to spray drying encapsulation (Benita, 1996).

### **3. Carrier solid**

The functional profile of carrier solid or wall materials that are optimal for spray drying includes a high solubility in water, a low viscosity at high concentrations and efficient drying properties (Madene et al., 2006).

Foods to be spray dried can be classified in two broad groups, non-sticky and sticky. In general, non-sticky material can be dried using a simple dryer design and the final products remain free flowing. On the other hand, sticky material is difficult to dry under normal spray drying conditions. Natural sugar and acid rich foods such as fruit and vegetable juices, and honey belong to this group. Stickiness is a major reason which has limited the use of spray drying for sugar-rich and acid rich fruits (Adhikari et al., 2004). Previous studies, Bayram et al. (2005) prepared spray dried Sumac extract, which contains malic acid, citric acid, tannic acid and gallic acid by using several carrier (sodium chloride, sucrose, glucose and starch). There found

that sucrose, glucose and starch were not suitable for spray drying of sumac due to their caramelization property and heterogeneous form.

Abadio et al. (2003) was studied effect of concentration of maltodextrin on physical properties of powdered pineapple. This study, pineapple was used spray dried with maltodextrin as carrier. The result of this study has shown significant effect on the moisture content. Increase in maltodextrin concentration resulted in decrease in moisture content.

In the study of mango pulp with vacuum drying, maltodextrin ranging between 0.25 and 0.65 kg per kg of mango solid was used. This result showed that maltodextrin could eliminate the stickiness of the mango powder and to get less hygroscopic powder (Jaya and Das, 2004).

Cano-Chauca et al., 2005 was study the induction of crystallization on mango juice powder during the process of spray drying and the correlation of the microstructure of the powder obtained with the functional properties of stickiness and solubility. In this study, mango juice with 12 °Brix was dried by spray drying method. Before being dehydrated, the juice was added to spray dried carrier with maltodextrin, acacia and starch waxy in the concentration of 12%. The microstructure analyses of spray dried powders showed that the powders of the mango juices obtained through spray drying using the carriers of maltodextrin, acacia, starch waxy without the addition of cellulose presented surfaces of amorphous particles. The value of stickiness decreased in terms of the concentration of cellulose reaching values of 0.15, 0.22 and 0.11 Kg-f for maltodextrin, acacia and starch waxy, respectively. The functional property of solubility is affected when 9% of cellulose is added reaching the values of 72, 71 and 31% for the carriers maltodextrin, acacia and starch waxy, respectively.

In the other studies about spray dried fruit juice, Mobhammer et al. (2006) were evaluated of different method for the production of juice concentrates and fruit powders from cactus pear, which rich both fructose and glucose. One of the method



for make fruits powder is spray-drying method. This study used maltodextrin as spray-dried carrier.

In addition to spray dried carrier such as acacia or maltodextrin, it is necessary to apply this technique to fruit juices, adding amounts not exceeding the operational limits of the equipment. Currently maltodextrin and acacia are the most widely used as spray dried carrier to obtain fruit juice powders.

### **3.1 Maltodextrins**

Maltodextrin are partially hydrolyzing corn flour with acid or enzyme. They are supplied with many dextrose equivalents (DEs), the DE value is a measure of degree of starch polymer hydrolysis.

#### **Typical properties of maltodextrin**

They occur as a non-sweet, odorless, white powder as granules. The solubility, hygroscopic and sweetness increase as the DE increases.

#### **(a) pH**

pH of maltodextrin at concentration 20% w/v solution in range 4.0-7.0 (Rowe, Sheskey, and Weller, 2003).

#### **(b) Solubility**

Maltodextrin are freely soluble in water; slightly soluble in ethanol. Solubility increases as dextrose equivalent DE increase (Rowe, Sheskey, and Weller, 2003).

#### **(c) Viscosity**

Viscosity of maltodextrin solution at concentration of 20% w/v is less than 20 mPas. The viscosity of maltodextrin solutions decrease as the DE increases (Rowe, Sheskey, and Weller, 2003).

**(d) Moisture content**

Maltodextrin is slightly hygroscopic at relative humidities less than 50%. At relative humidity greater than 50%, the hygroscopicity of maltodextrin increase nonlinearly (Rowe, Sheskey, and Weller, 2003).

In selecting carrier of spray drying, maltodextrin have low viscosity at high solid ratio and it available in difference average molecular weights. Further more, maltodextrin is a good compromise between cost and effectiveness (Madene et al., 2006).

**3.2 Acacia**

Acacia or Gum Arabic is a complex, loose aggregate of sugars and hemicelluloses with a molecular weight of approximately 240,000-580,000. The aggregate consist essentially of and Arabic acid nucleus to which are connected calcium, magnesium, and potassium along with the sugars arabinose, galactose and rhamnose.

**Typical properties of acacia****(a) pH**

pH of acacia solution at concentration of 5 %w/v is in range 4.5-5.0 (Rowe, Sheskey, and Weller, 2003).

**(b) Solubility**

Acacia is soluble 1 in 20 of glycerin, 1 in 20 of propylene glycol, 1 in 2.7 of water and practically insoluble in ethanol (95%) (Rowe, Sheskey, and Weller, 2003).

**(c) Viscosity**

Aqueous acacia solution in concentration 30% w/v gave viscosity of 100 mPas at 20°C. The viscosity of aqueous acacia solution varies depending upon the source of the material, processing, storage conditions, pH, and the presence of

salts. Viscosity increases slowly up to about 25% w/v concentration and exhibits Newtonian behavior. Above this concentration, viscosity rapidly increases (Non-Newtonian rheology). Increasing temperature or prolong heating of solution results in a decrease of viscosity due to depolymerization or particle agglomeration (Rowe, Sheskey, and Weller, 2003).

#### **(d) Hygroscopicity**

Acacia at relative humidity between 25-65 % the equilibrium moisture content of acacia powder at 25°C is between 8-13 %w/w, but at relative humidity above about 70 % is absorbs substantial amounts of water (Rowe, Sheskey, and Weller, 2003).

Acacia is most often used as encapsulation wall material because of its solubility, low viscosity property at high concentration in feed (Madene et al., 2006).

## **F. EMULSIONS**

### **1. Definitions/Types**

Emulsion are heterogeneous system consisting of at least one immiscible liquid that is intimately dispersed in another liquid in the form of droplets, or “globules,” whose diameters generally exceed 0.1  $\mu\text{m}$ . Emulsion are also defined as thermodynamically unstable mixtures of two essentially immiscible liquid and an emulsifying agent to hold them together. The process of combining these ingredients is termed emulsion.

An emulsion consist of a dispersed phase (internal phase or discontinuous phase), a dispersion medium (external phase or continuous phase), and a third component, known as an emulsifying agent. The diameter of the dispersed-phase globules is generally in the range of about 0.1 to 10  $\mu\text{m}$ , although some can be as small as 0.01  $\mu\text{m}$  or as large as 100  $\mu\text{m}$ .

Emulsions are used as a dosage form whenever two immiscible liquid must be dispensed in the same preparation. Ordinarily, the mixture has both a polar and a non polar component, each of which is a liquid. When the dispersed phase is non polar (oil) and the dispersed medium is polar (water), the emulsion is known as an oil-in-water (o/w) emulsion. When the dispersed phase is water and the dispersion medium is oil, the emulsion is of the water-in-oil (w/o) type. Generally, emulsions for internal use are the o/w type, and those for external use can be of either type. Water-in-oil emulsions are insoluble in water, are not water washable, will absorb water, are occlusive, and can be "greasy." Conversely, o/w emulsions are miscible with water, are water washable, will absorb water, are nonocclusive, and are non-greasy.

Creams are opaque, soft solids or thick liquids consisting of medications that are dissolved or suspended in water-removable (i.e., vanishing cream) or emollient bases. They are intended for external application and can be either type of emulsion. The term "cream" is often applied to soft, o/w, cosmetically acceptable types of preparations. Cream are usually applied to moist, weeping lesions because they have a somewhat drying effect in that lesion' fluids are miscible with the aqueous external phase of creams.

Lotions are fluid emulsions or suspensions designed for external application. They have a lubricating effect and thus are applied to intertriginous areas, that is, areas where the skin rubes together, such as between the fingers, between thighs, or under the arms.

## **2. Historical Use**

The term "emulsion" is derived from the word "emulsus." The verb associated with this word, "emulgere," mean "to milk out." Emulsion originally referred to the milky liquid extracted from almonds but in time was used to refer to any milky fluid. Although emulsions still have milky appearance, the term now commonly refer to a dispersion of immiscible liquids (Young, 2002).

### 3. Applications

Topical creams and lotions are popular forms of emulsions for external use. Internally, emulsions are used to dispense oil and aqueous drugs together, to mask the taste of unpleasant oily drugs and sometimes to enhance the absorption of selected drugs. Emulsions containing high caloric oil can be administered intravenously to severely debilitated patients (Young, 2002).

### 4. Composition

Emulsions generally contain three components: a liquid phase, an aqueous phase, and an emulsifier. The compounding pharmacist has greatest flexibility in the choice of an emulsifier. Common emulsifiers are listed in Table 2 (Young, 2002).

Table 2 Emulsifiers and Stabilizers Used in Emulsions (Young, 2002).

<b>Carbohydrates</b>	<b>High Molecular Weight Alcohols</b>
Acacia	Cetyl alcohol
Agar	Glyceryl monostearate
Chondrus	Stearly alcohol
Pectin	<b>Surfactant</b>
Tragacath	Anionic
<b>Proteins</b>	Cationic
Casein	Nonionic
Egg yolk	<b>Solids</b>
Gelatin	Aluminum hydroxide
	Bentinite
	Magnesium hydroxide

### 5. Preparation

Emulsions do not form spontaneously when liquids are mixed. Rather, they require energy input, such as mechanical agitation, ultrasonic vibration, or heat, to break up the liquids, which thereby increases the surface area of the internal phase.

Emulsions can be prepared by both manual and mechanical methods. These methods can involve the use of a mortar and pestle, a bottle for shaking, beakers, mortar and pestle can be used with both the English and the Continental methods of emulsification, which are described later. For best results, the mortar should have rough surfaces to help shear the liquid into small globules.

The English method, also called the wet gum method, relies on the use of mucilages or dissolved gums. The ratio of oil: emulsifier often ranges from 2 to 4:1 for forming the primary emulsion, as shown in table 3. The mucilage is made by adding a small quantity of water to the hydrocolloid (e.g., acacia) and then triturating the mixture until uniform. Oil is added in small quantities by using added slowly, and the emulsion is triturated rapidly until complete (Young, 2002).

Table 3 Component Ratios for the Preparation of Primary Emulsions (Young, 2002).

<b>Oil</b>	<b>Acacia</b>	<b>Tragacanth</b>
Fixed oils	4:2:1	40:20:1
Mineral oil	3:2:1	30:20:1
Linseed oil	2:2:1	20:20:1

The Continental method, known as the dry gum method, involves rapid mixing of the hydrocolloid with the oil for a short time, after which the water is added all at once with rapid trituration. When a snapping sound is heard, the primary emulsion has formed. More water is then added slowly with rapid trituration until the emulsion is complete. The ratio of oil:water::emulsifier for preparing the primary emulsion is generally about 4:2:1.

The bottle method (shaking) is another approach to preparing emulsion that contain volatile oils and other nonviscous oils. This method eliminates the splashing problem that sometime occurs when a mortar and pestle are used. The bottle method, which is a variation of the dry gum method, involves mixing the powder (emulsifier) and oil in a bottle and then shaking the bottle with short, rapid movement.

The required quantity of water is added all at once, and mixture is again shaken rapidly to form the primary emulsion (4:2:1 ratio). If more water is require, it is added in small amounts, with the bottle shaken after each addition. The oil and gum should not be allowed to remain in contact too long, as the gum can imbibe the oil and partially waterproof the powder.

The beaker method is often used with synthetic emulsifying agent. The prescription ingredients are generally divided into two separate phase: oil and water. Each phase is heated individually to about 60°C to 70°C, if needed. The internal phase is then stirred into the external phase. Finally, the product is removed from the heat and stirred gently and periodically until it has cooled (congealed).

A mechanical stirrer (mixer) with various impellers can be used to prepare an emulsion. The unit's propeller should be placed directly into the system to be emulsified. Mixers are available commercially and can be found in department stores and gourmet kitchen stores.

Hand homogenizers function by forcing the mixture of liquids though a small inlet orifice at a high pressure. This shearing action causes the globules to break up (Young, 2002).

## **6. Incorporating materials into a w/o emulsion**

Oils and insoluble powder can be incorporated directly into on emulsion by using a pill tile and spatula or a mortar and pestle. A levigating agent may be needed if large amounts of insoluble powders are required are for the formulation. In many w/o emulsions, sufficient emulsifying agent is available to emulsify a larger quantity of the aqueous solution of the drug, which can be incorporated by using a pill tile with a spatula or a mortar and pestle or gentle heat from a water bath. When using heat, the pharmacist should make sure that the preparation is not held at a high temperature or too long because some loss of water can occur. This loss of water would change the volume of the product. Adding oily ingredients usually poses no problem. Some crystalline drugs may need to be dissolved in oil before being

incorporated, if possible. In this case, it may be necessary to the base form rather than the salt form of the drug. Adding water to these emulsions is difficult unless an excess quantity of the emulsifier is present (Young, 2002).

#### **7. Incorporating materials into an o/w emulsion**

A pill tile and spatula or a mortar and pestle are also used to incorporate insoluble powders and aqueous solutions into emulsions. It may be advisable to use a levigating agent, such as glycerin or propylene glycol, when mixing the insoluble powder with the emulsion. Crystalline materials should be dissolved in a small quantity of water before they are added to the emulsion. Water-soluble materials should also be dissolved in a small amount of water before the solution is incorporate into the base. Because there is usually an excess of emulsifying agent, a small quantity of oil can be incorporate directly into the base. However, if larger amounts of oil are required, it may be necessary to add a small quantity of an o/w surfactant to help disperse the oil uniformly in the vehicle. It is generally easy to add water-soluble ingredients.

Using heat to incorporate an ingredient into an o/w vehicle can cause the product to lose water. Thus, it is necessary to work quickly. If water is lost, the volume of the product will change; moreover, if it is a semisolid, it may tend to become stiff and “waxy” (Young, 2002).

#### **8. Evaluation of emulsion stability**

Emulsion stability may be assessed after storage of the product for the proposed shelf-life; this, however, is time-consuming and most workers rely on accelerated tests to provide information on long-term stability. Accelerated tests involve placing the emulsion under stress; this is normally applied using agitation, centrifugation, or temperature manipulation techniques.

Agitation increases the rate at which droplets meet and therefore decreases the time-scale over which collisions occur.



Centrifugation rapidly induces creaming or coalescence in potentially unstable systems. Conditions should be carefully chosen to prevent distortion of the droplets or disruption of the interfacial film.

Temperature manipulations, such as alternating between high and low temperatures, are the most commonly employed type of accelerated stability tests. Extremes of temperature, however, should be avoided (Lund, 1994).

Various physical parameters, appearance such as phase separation, color, odor, pH, viscosity, and strength, are used to monitor the stability of emulsion during these tests. Storage on the side or inverted is suggested for assessment of the closure system. It is recommended that a heating/cooling cycle be employ (e.g. between 4 °C and 45 °C) (Carstensen, 1995).