CHAPTER 2

LITERATURE SURVEY

2.1 Ball clay and refined ball clay in Thailand

There are many ball clay resources[1,2] in Thailand, scattering from northern, middle to southern parts of the country. Northern ball clays are Lampang ball clay from Ban Jae Korn and brown ball clay from Ban Mae Than where is the largest clay production area. The others are Chiangmai ball clay for celadon and roofing tile industries. Ball clays in the middle and eastern parts of Thailand are in Pracheanburi and Chantaburi Provinces. Southern ball clays were found in the areas of Amphur Nasarn, Viensah, Kanchanadith, Suraj Thani Province and neighborly in Nakornsrithammarat Province at Amphur Chawang, Pipoon, Lansaka, Ron Phibun (tumbol Kok Kharm) and Sichon. The other provinces are Yala, Narathiwat and Phuket.

Some northern ball clays have fine grains, slippery surface, high fired strength and are white in fired color. The outstanding source is Jae Korn ball clay of which properties are suitable for casting application. Mae than ball clays have variety of colors. Some white and yellow Mae Than ball clays are suitable for tile industries. Brown or black Mae Than ball clays have high plasticity and are widely used for sanitarywares and insulators.

Ball clays from southern part of Thailand have high plasticity and fine grains suitable for production of tablewares and insulators. Southern

ball clays have a better fired color in reducing atmosphere than some northern ball clays although they have higher Fe_2O_3 content. This is because they have lower TiO_2 content.

Table 2.1 Chemical composition and mineral composition of Thai ball clays.[2]

Ball clay source	Jae Korn Lampang	Mae Than Lampang	Na Sarn Suraj Thani
Chemical composition % SiO_2	52.6	62.3	56.5
% Al_2O_3	29.8	24.50	28.4
% Fe_2O_3	2.09	1.22	1.88
% TiO_2	0.63	0.57	0.22
% CaO	0.40	0.24	0.31
% MgO	0.74	0.59	0.31
% K_2O	2.78	2.14	2.28
% Na_2O	0.85	0.13	0.16
% LOI	7.04	8.31	9.90
Mineral composition Quartz (%)	15	28	5-6
Major	Very disordered kaolinite or Chlorite	Disordered kaolinite	Very disordered kaolinite
Moderate	Illitic mica	Illitic mica	Illitic mica
Minor	Hematite	Montmorillonite	Feldspar

Table 2.2 Particle size distribution, some physical and rheological properties of Thai ball clays.[2]

Ball clay source	Jae Korn Lampang	Mae Than Lampang	Na Sarn Suraj Thani
Particle Size Distribution +125 μm	0.21%	3.1%	4.9%
- 20 μm	98%	95%	93%
- 10 μm	96%	94%	84%
- 5 μm	94%	85%	79%
- 2 μm	89%	65%	73%
- 1 μm	79%	50%	69%
-0.5 μm	64%	36%	66%
Physical and rheology properties Volume drying shrinkage (%)	34	23	29
MOR (kg/cm^2)	140	53	103
Fired color at 1200°C (Whiteness)	25.6	87.0	54.2
Deflocculant demand (%)	1.25	0.85	0.90
At ball slip density (kg./l.)	1.502	1.600	1.55
Solid content of ball slip (%)	48.5	62.6	52.5

Ball clay occurs as sedimentary deposits which have traditionally been supplied to whitewares industry with a minimum of processing. Cubes of clay are cut from seams, weathered and then sold in form of large rounded lumps. Some of clays are blended for producing a range

of products more cost efficiency and with greater variety of ceramics properties. The cost is relatively inexpensive but impurities are hard to control.

Refined ball clay is another alternative for ceramic industries because of superior consistency. Unpublished information from ball clay distributors refers that refined ball clays consumed in Thailand are around 150-200 tons per month. Main refined ball clay producers are Compound Clay Co., Ltd. and Clays and Minerals (Thailand) Ltd. They supply refined ball clay in filter cake form to Thai tile factories for engobe work and export to some Asian countries. Exported refined ball clays are about 100 tons per month.

2.2 Commercial refined ball clay[3]

Asian countries, included Thailand, consume commercial refined ball clays from England. Resources[3] of these ball clays are in the regions of south Devon, north Devon and Dorset. The most plastic, low residue, generally non-carbonaceous types are found in Dorset, but the good casting types are mostly in south Devon. The main suppliers are ECC International and the International Watts Blake Bearne Group (WBB). Refined ball clay products of each company are different in both process and trade name character. WBB products are mostly semi-refined clays, mixture of raw clay with refined one in noodle or air float type. The most popular grade is Sanblend 75 for Asian and European sanitaryware industries. Whereas ECC International produces fully refined ball clays in powder, pellet, shredded or spray dried granule forms.

Sanitaryware industries in Thailand prefer to use refined ball clays that have good rheology, casting properties and high plasticity, mostly imported in noodle or pellet types but tile factories in Thailand prefer imported refined ball clay in form of spray dried granule, Hypure Vector®, from England, 40-60 tons per month.

2.3 Granulation and Spray drying[4,5]

Granulation is the intentional agglomeration of fine particles into larger clusters in order to improve certain powder properties. Granulated powders used in the ceramic industry are typically used as feedstock for either a shape forming technique, such as powder pressing, injection molding, or extrusion, or a thermal treatment operation. The intended use of granulated powder dictates the properties that are most important, therefore the optimum granulation must be chosen. The granulation methods used by the ceramic industry can be categorize as agitation, pressure or spraying techniques. All of these methods use powder mixed with liquid such as water or binder solution.

Spray drying is the most common granulation technique for producing ceramic press-powders which has different method or contrary way to the three former techniques. The feed is usually a water or liquid based suspension, called a slurry, and the drying medium is heated air. The slurry is pumped to an atomizer located in drying chamber, where it is broken into a large number of droplets. These droplets quickly achieve a spherical shape because of surface tension effects. The large surface area-to-volume ratio of the droplets allows rapid water evaporation and the resulting dry powders are separated from the hot air and stored for future use.

Spray drying has long historical background. Industrial applications occurred first in milk and detergent in the 1920s but spray drying concepts were known before this date. Mr. Samuel Percy[6], who was considered the first to have described in detail of drying products in spray form registered his patent – Improvements in drying and concentrating liquid substances by atomizing – in 1872. Nowadays, spray drying is significantly applied to various industries.

2.3.1 Advantages and disadvantages of spray drying

With spray dryers operating in industries that range from aseptic pharmaceutical processing, food industries at a few kilograms per hour through over than 100 tons per hour in chemical fields as mineral ores and clays in ceramic industry, there are many advantages that have led spray drying to be the most important industrial drying system.

Advantages of spray drying

1. Powder quality remains constant throughout the entire drying operation.

2. Spray dryer operation is continuous and easy. Operation is adaptable to full automatic control.

3. Dryer designs are available in a wide range.

4. Spray drying is applicable to both heat-sensitive and heat-resistant materials.

5. Feedstocks in solutions, slurry, paste or melt forms can be handled if pumpable.

6. Spray dryers can be designed to any capacity requirement.

7. There is extensive flexibility in spray-dryer designs to handle drying of toxic materials, drying of materials that gives odour discharge,

evaporation of organic solvent-based feedstocks without explosion and drying of feedstocks that require aseptic/hygienic drying conditions.

*Disadvantages of spray drying*

1. Installation costs are high. Industrial units are big and tall in order to obtain more powder output for running process.

2. Larger units require expensive buildings and/or supporting structures.

3. In high temperature spray drying is possible to cause the product heat degradation effects.

4. Spray drying requires sophisticated heat-exchanger design to remove large amounts of low grade waste heat.
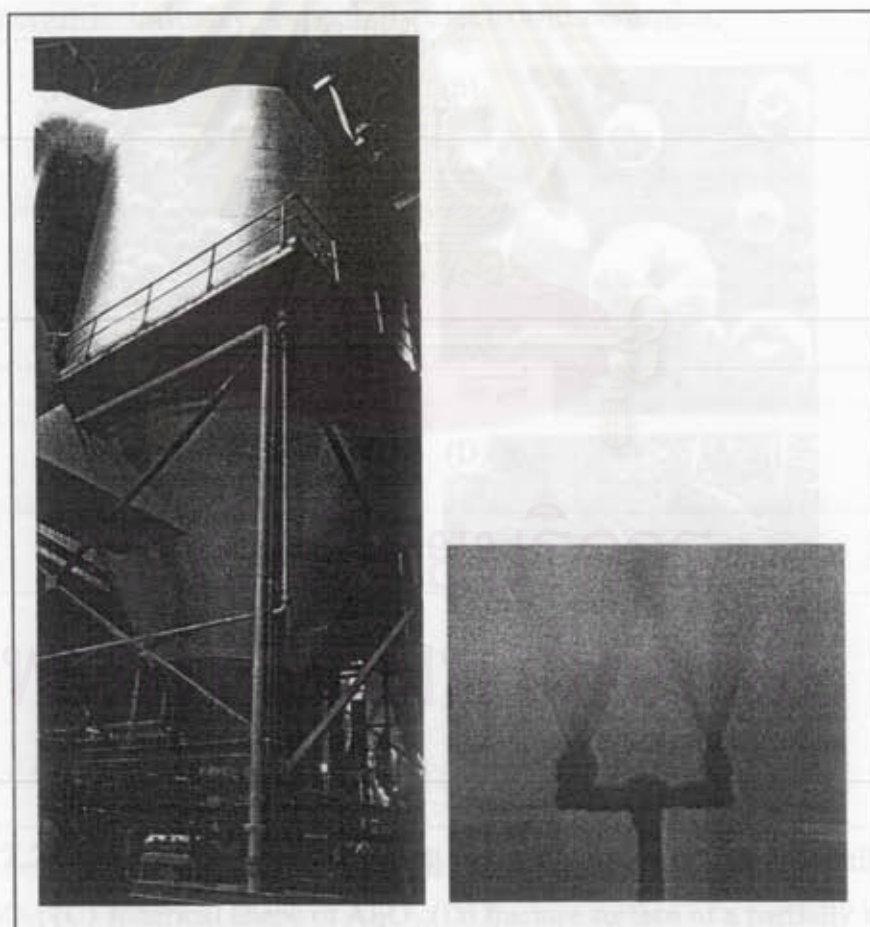
Fig. 2.1 Spray dryer in production scale.(ECC International LTd,1996.)

2.3.2 Spray-drying ceramic powders[7]

Spray drying is the ideal processing technique to produce powder characteristics according to the manufacture of ceramic products involving preparation of raw materials in a slurry form, drying, pressing prior to firing and the final processing stage. Characteristics of the powder are free-flowing and homogeneous features effect on the quality of finished products. Granulation by spray drying is used in manufacture of whitewares, electronic ceramics and structural ceramics. The growth of spray drying application within whiteware manufacture was most widespread in the 1950s to 1970s. Nowadays, the area of advanced ceramics gives the most significant potential for spray drying in the overall ceramic industry, especially electronic ceramics.
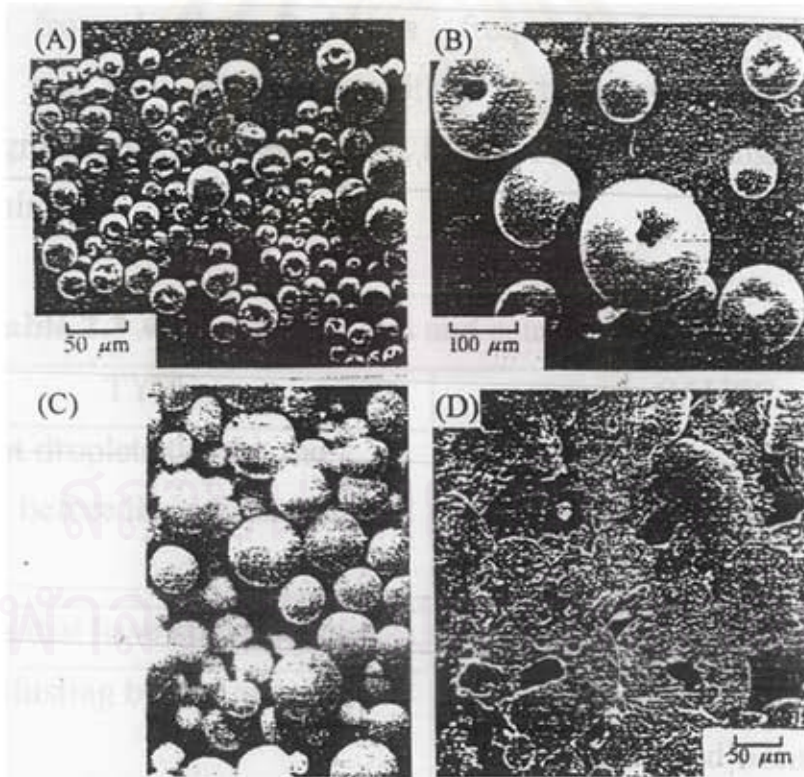
Fig. 2.2 Commercial spray drying ceramic powders: (A) $MnZnFe_2O_4$; (B) Al_2O_3; (C) spherical shape of Al_2O_3;(D) fracture surface of a partially sintered compact of the Al_2O_3 in (B)-showing the internal structure of the granules.[5,6]

2.4 Spray drying fundamental [5,6,7,8]

Process of spray drying includes four stages;
a) *Atomization of feed into a spray*
b) *Spray-air contact (mixing and flow)*
c) *Drying of spray (moisture/volatile evaporation)*
d) *Separation of dried product from the air*

Each stage is carried out according to physical and chemical properties of feed, dryer design and operation which determine the characteristics of the dried product. The rapid mass transfer which occurs during drying and the presence of various slurry additives, especially organic binders, can result in the dry granule having shape and size different from droplets. Problems frequently found such as hollow granules and wall deposits, resulting in large compaction ratios and density gradients in pressed article, increase manufacturing cost and time for cleaning.

Table 2.3 Wall deposit types and causes.[4]

| TYPE	CAUSE
Semi-wet droplets that hit the chamber before their surface dry	Large droplet size, incomplete atomization improper air flow, and low-solid-content slurry
Granules that have sticky surface	Function of organic additives
Surface dusting by dry granules	Wall geometry and cleanliness, local air flow conditions, electrostatic forces, and low-density granule
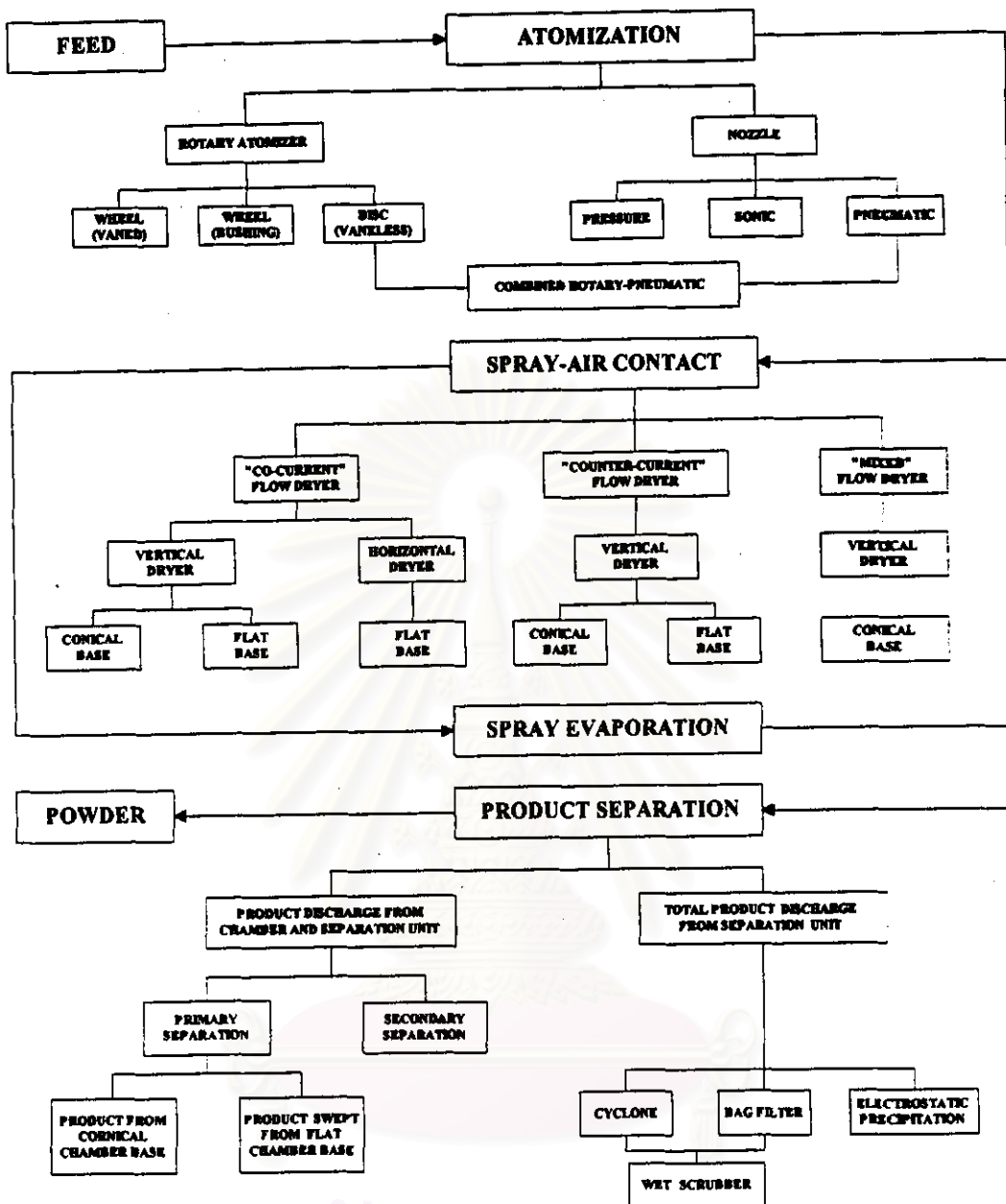
Fig. 2.3 The features of the process stages involved in spray drying (shown diagrammatically)[6]

2.4.1 Slurry preparation[5]

Preparation of slurry is normally not considered as a part of the drying operation but it is the main factor which effects the character of

the granules and the dryer operation. Most spray-dried ceramic powders are produced from water-based slurries, limited to such systems. If the slurry is formulated with flammable or explosive liquid, closed-cycle dryers that use nitrogen as the drying medium are required.

The slurry is prepared by dispersing the ceramic powder in water. Any aggregates present should be eliminated through a milling or screening procedure. A high weight percent solid slurry is usually desired because it results in a higher powder output rate from a dryer with a given evaporative capacity. From Fig. 2.4[5], increasing the weight percent solids from 50% to 75% will triple the powder output if no operational difficulties are caused by the increased solid content.
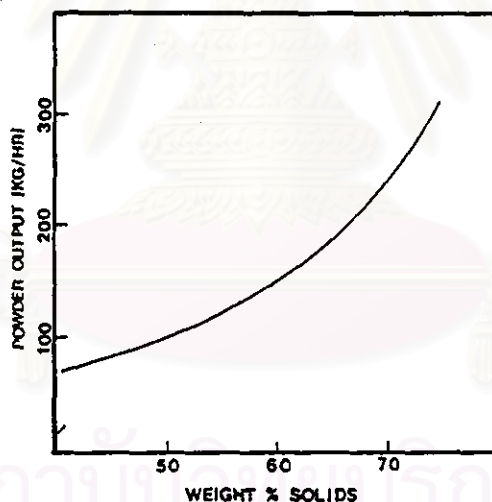
Fig. 2.4 Powder output from a spray dryer as a function of the weight percent solids in the feed slurry.

Dryer evaporative capacity is 100 kg/h. of water and a yield of 100% is assumed. [5]

However, as solid content increases, slurry viscosity also increases and mixing becomes difficult. To maintain a low viscosity, the system must be deflocculated. Dispersants used in ceramic slurries are typically

organic polymers but inorganic dispersant such as sodium silicate is widely used in some industries because of less price. Spray-dried powders usually contain 0.5 to 4.0 wt % binder, based on the dry weight of ceramic powder. Binder is necessary to clay-free ceramic powders to provide green strength for pressing. The method of adding binder to the slurry is considerably important. Binder addition as a prepared solution is desirable in consistent with the required solid content to remove undissolved or undispersed organic material preliminarily. Because the presence of organic agglomerates will impart defects to the fabricated articles.

2.4.2 Atomization[5,6]

The atomization stage is central to the spray drying process, and successful operation is impossible without effective slurry atomization. Atomization of the ceramic slurry generates a large number of small droplets from bulk fluid and results in a large increase in the surface area-to-volume ratio, equal to 6/d where d is the droplet diameter, allow rapid moisture removal.

In ceramic drying, The choice of atomizer type depends upon the slurry character, the desired droplet size distribution and the required drying capacity. Atomizers can be classified according to the manner in which energy is supplied to produce these droplets. The three most common types are rotary atomizers (centrifugal energy), pressure nozzles (pressure energy) and pneumatic nozzles (kinetic energy).
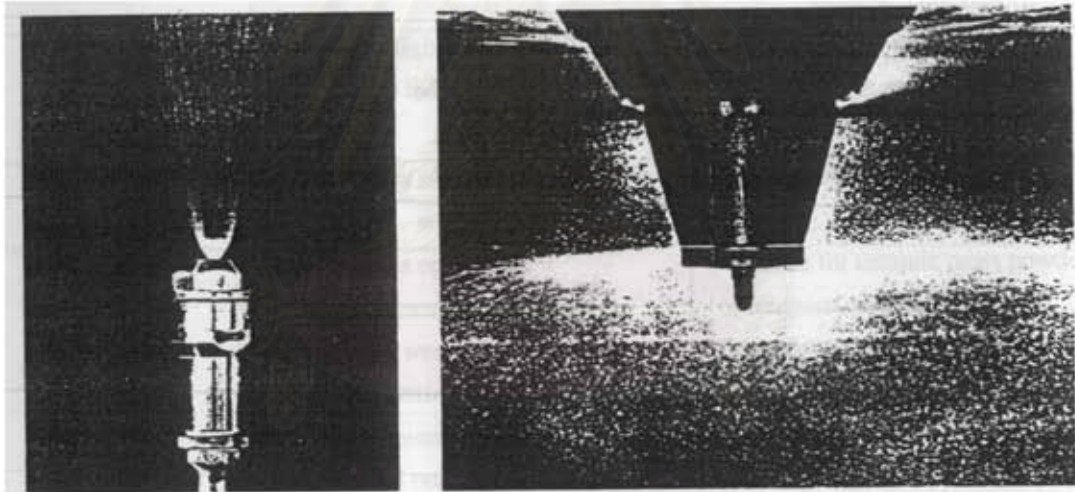
Rotary atomization

A rotary atomizer consists of a spinning wheel or disk centrally located in the upper portion of the drying chamber and rotating at speed up to 20000 rpm.[8] The slurry is pumped to the atomizing device at pressures less than 690 kPa (100 psi) and is accelerated outward into the chamber. It disintegrates into droplets because of frictional forces between the airborne liquid and the drying air. Various wheel and disk designs have been developed for controlling different droplet size distributions. The particle size of ceramic powders produced in spray dryers with rotary atomizers increases with decreasing in atomizer wheel speed (constant wheel diameter) or diameter, increasing feed rate and slurry viscosity. The effect of feed rate is not great within optimum working range of the given atomizer wheel.[7]

Pressure atomization

Pressure nozzles atomize the slurry by accelerating it through a large pressure differential and injecting it into the drying chamber at high velocity. Flow rate of the slurry is limited by the size of the nozzle and is proportional to the pump pressure. Since this is a high pressure technique, the feed pumps are relatively expensive and difficult to maintain. The nozzles are inexpensive but can cause significant variation in droplet spray patterns due to even slight wear. Subsequently results of droplet variation are a non-uniform spray pattern and a chance to stick on the chamber wall. The drying chambers are characteristically long because the droplets exit the nozzle with a high velocity. Granule size is proportional to slurry viscosity and orifice diameter but inversely to pump pressure.[4]

Pneumatic atomization

Pneumatic atomization occurs when the feed is impacted by a stream of high velocity air. This can happen within the nozzle (internal mixing) or after the slurry is ejected from the nozzle orifice (external mixing). Internal mixing nozzles have greater energy efficiency and produce a more uniform droplet size, but they do not have adaptability of external mixing unit where both of the feed rate and the air flow can be adjusted over a wider range. Pneumatic nozzles operate well at low feed rates and can handle both low and high viscous slurries and be often used in laboratory size dryer. Granule size increases with increasing slurry viscosity, decreasing velocity between the atomizing air and the slurry.

(a)   (b)

Fig. 2.5 Atomizers used in spray drying ceramics : (a) hydraulic pressure nozzle; (b) rotary (wheel) atomizer [7]

Table 2.4 Comparison of centrifugal and nozzle atomization in spray dryers.[8]

Type of atomization	Centrifugal Atomization (Rotary Atomizer)	Nozzle Atomization (Pressure Nozzle)
Diameter of atomizer	5-15 in. diameter of disk 5000-20000 rpm.	Orifice 2-3 mm. in diameter
Pressure pump	50 psi	150-750 psi
Atomizer assembly	In the top-center of the drying chamber	In the cone of drying chamber
Granule size distribution	Uniform spheres with narrow size distribution for isostatic pressing	A wider size distribution and larger average particle size
Spray-Air contact	Co-current pattern	Counter-current pattern
Discharged granule temperature	25-75°F less than the outlet air temperature. More number of additives available	275-300°C close to outlet air temperature. Partially dried granules exposed to inlet temperature can be affected heat sensitive additives
Feed rate	Higher feed rate, 750-2500 lb/h depend on product quality	25-500 lb/h depend on product quality
Maintenance cost	Spare parts of atomizers and disks are needed	Spare parts of feed pumps are needed
Advantages/ *Disadvantages*	-continuous operation -low maintenance cost -minimize wear of disk and proper size distribution -only one atomizer can be used for whole feed rate to 20,0000 lb/h -turndown capability by reduction in disk speed -possible to control inlet/outlet temp. by regulating the fuel rate and feed rate	-suitable for ceramic press powder of tungsten carbide because of limitation of the explosive and milling liquid (hydrocarbon base) -dry product collection >95% *-nozzle plugging and wear* *-large capacity requires multiple nozzles* *-difficult to maintain equipment* *-turndown capability of nozzle is less than centrifugal atomizer* *-impossible to control inlet/outlet temp by fuel rate because of the constant feed pressure requirement*

2.4.3 Spray-Air contact [5,6]

The spray of droplets mixes with the hot drying air entering through the air disperser and can be classified according to the relative directions in which the atomized spray and the drying air traverse the drying chamber. These classifications are terms of co-current, counter-current and mixed-flow mixing.

(a) Co-current   (b) Counter-current   (c) Mixed-flow
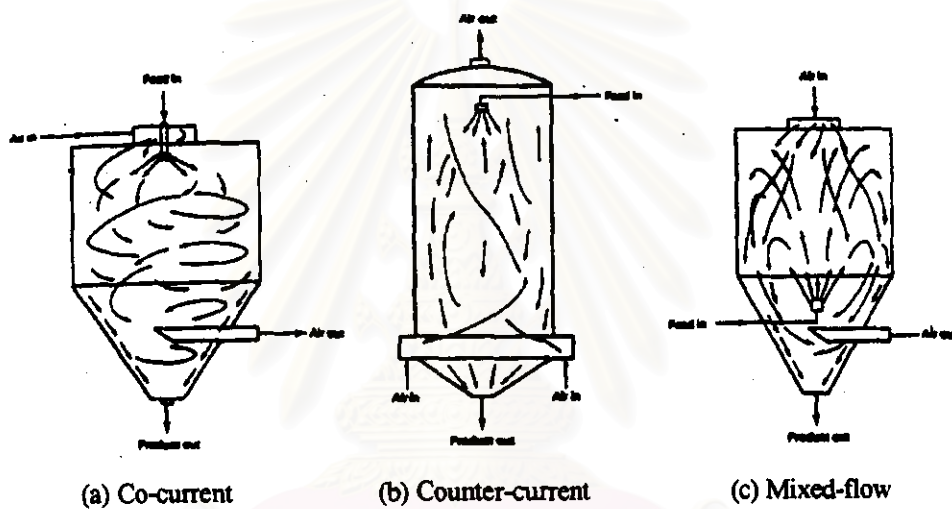
Fig. 2.6 Droplet-Air mixing types common used in spray dryers[4]

Co-current

The atomizing device is located near the air disperser at the top of drying chamber. The droplets are exposed to the hottest air suddenly after atomizing and have high evaporation rate to maintain low product temperatures. They come into cooler part while the moisture content of droplets decreases. Co-current air flow is normally equipped with rotary atomizers.

Counter-current

The atomizing device is placed at the top of drying chamber while the air disperser is placed at the bottom. Direction of droplets is opposite to the air flow. The droplets immediately contacts cool, humid air after formation and comes into contact with hotter air before exiting the dryer. Granules will have high surface temperature, the organic binders should not be heat sensitive.

Mixed-flow

Mixed flow simply combines co-current with counter-current conditions. This type is installed in 'fountain type' dryers where the nozzles are placed at the base of the chamber, atomize a fountainlike spray, whereas the drying air inlet is located at the top of chamber. The initial droplet-air mixing is counter-current. Production of coarse powders in a mixed flow drying with nozzle atomizer requires a smaller diameter size of chamber than the size required for a co-current drying with rotary atomizer for the same capacity.[7]

The way in which spray contacts the hot drying air is a significant factor in spray dryer design because the air flow has a large effect on droplet behavior during drying as droplet drying time, in the chamber, moisture removal and the formation of wall deposit.

2.4.4 Drying of Spray [5,6]

As the feed is sprayed into the hot air, droplets immediately establish a saturated vapor film at the surface of each droplet in the spray. Evaporation takes place after entering the chamber, the droplet

achieves its maximum rate, called the constant rate drying period (curve B-C), continues as long as moisture can migrate from droplet interior to the surface rapidly enough to maintain entire surface saturation. This constant period depends on the droplet moisture content, viscosity of migrating liquid, temperature and humidity of the drying air. At point C, the critical moisture content, the entire droplet surface can no longer maintain surface saturation and the falling rate drying period begins (curve C-E). The droplet temperature will begin to increase as its evaporation rate decreases. Point D, the entire surface is saturated and drying rate continues to decrease as the plane of evaporation moves inside the droplet, the droplet is now surrounded by a Solid Crust and further removal of water is function of the moisture permeability of this crust.
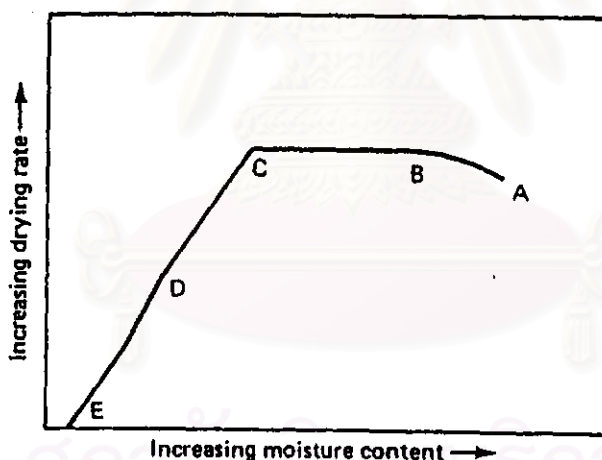
Fig. 2.7 Evaporation behavior of an atomized droplet.[5]

Hollow granules [4, 5]

Four possible mechanisms of hollow granule formation are:

- A low permeability film layer forms on the droplet. Evaporation

of moisture occurs within the droplet interior and increases droplet temperature and causes the "balloon" surface.

- Moisture migrates to the droplet surface, where evaporation and soluble salt crystallization happen. The rate of evaporation exceeds the diffusion rate of salt back into the droplet interior and voids are formed inside the granules.

- For slurry of insoluble solids, particles are carried along as liquid flows to the droplet surface under capillary action. The liquid evaporates and internal voids result in the granules.

- Air trapped in the feed slurry is incarporated with atomized droplets and retained in granules.

In the absence of film formation, a high-solid-content slurry will result high-density granules. Because the amount of water decreases. Particle migration is impeded and intervoid volume is minimized.

Binder migration

Organic binders, especially water soluble types, have a trend to follow moisture flow during droplet drying. The binder migration causes nonuniform distribution of organic in spray dried granules and results in an increased binder concentration on the granule surface. Granules will have a tough surface layer that resists deformation during compaction. The binder migration to the surface will be minimized corresponding to a short constant rate drying period.

2.4.5 Separation of dry product from the air[6,7]

The Final stage is the separation of granule from the exhausted air. All of the granules can be removed from the base of the drying chamber continuously, coarse and fine fractions can be separated and collected individually.

Two systems are used in ceramic drying.

a) Two point discharge, primary discharge of the coarser fraction is achieved from the base of the chamber while the finer fraction is collected from the cyclone or the bag collector.

b) Single-point discharge, where the total recovery of dried product is accomplished in the dryer separation equipment, i.e. cyclones. The finer particles are required at low production rate.

2.5 Effect of organic binder on Characteristics of Granule

Organic binder is one of the additives widely used in ceramic processing. The main purpose of the binder is to provide green strength for maintain the shape until it is sintered. In some other situation where not much green body strength is needed, the solvent alone has enough surface tension to bind the powder particles together sufficient to keep the body damp, examples are wet clays in the manufacture of simply shapes.[9] The more surface area, the more strength and some extra fine clay can be added for making roof tiles, rectangular bricks or drain pipes. However, only wet strength is too limited for other applications. Most modern process use of additional synthetic or other binder to improve the strength further and lessen the lot to lot variation found among the natural clays.

Desirable Characteristics of Binder

- Easy burn out
- Strong green body
- Solubility in fluidizing liquid
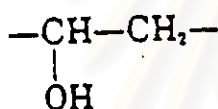- Low cost
- Insensitive to environmental condition

Table 2.5 Common binder choices[9]

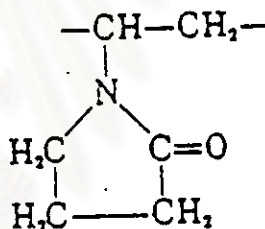| Application	Binders	Advantages
Slip Casting	Strach	Inexpensive
	Sodium Lignosulfonate	Inexpensive
	Na Carboxymethyl Cellulose	Inexpensive
	Sodium Silicate	Strong
	Ammonium Polyacrylate	High Solids
Tape Casting	Polyvinyl Butyral*	Strong
	Methacrylate Sltn. (in MEK)*	Easy burnout
	Methacrylate Emulsion	Easy burnout
	Ammonium Polyacrylate	High Solids
Extrusion	Methyl Cellulose	Heat-Gelation
	Starch	Inexpensive
	Sodium Silicate	Strong
Injection Molding	Wax and Polyethylene*	Easy burnout
	Epoxy or Phenolic*	Very Strong
Dry Pressing	Polyvinyl Alcohol	Plasticizable
	Methacrylate Emulsion	Easy burnout
Screen Printing	Alginates	Inexpensive
	Gums	Inexpensive
	Ethyl Cellulose*	Pseudoplastic
	Polyvinyl Butyral*	Easy burnout
Glaze Coating	Gums	Inexpensive
	Na Carboxymethyl Cellulose	Inexpensive
	Sodium Silicate	Strong

* Nonaqueous. (The others are aqueous.)

Note: Sodium compounds leave residue after burnout, and sodium silicate leaves even more residue.
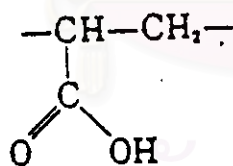
Most soluble organic binders are long chain polymer molecule. The backbone of the molecule consists of covalent bonded atoms such as carbon, oxygen and nitrogen. Side groups attach to the backbone located at frequent interval along the length of molecule. The side group determines in part of solubility in liquid. The long-chain molecules of binders consist of smaller units, called monomer that are linked together. The number of monomers in a polymer is called the "degree of polymerization". Some binders are characterized by a ring-type monomer. The monomer formulas for some important binder that are not of vegetable origin. These include the vinyls, acrylics and polyethylene oxides.[10]

$$-CH-CH_2-$$
$$\quad\ \ |$$
$$\quad\ \ OH$$

Poly(vinyl alcohol)

$$-CH-CH_2-$$
$$\quad\ \ |$$
$$\quad\ \ N$$
$$H_2C \qquad C=O$$
$$\ |\qquad\qquad |$$
$$H_2C——CH_2$$

Polyvinylpyrrolidone

$$-CH-CH_2-$$
$$\quad\ \ |$$
$$\quad\ \ C$$
$$\ \ //\quad \backslash$$
$$O\qquad OH$$

Poly(acrylic acid)

$$\qquad CH_3$$
$$\qquad |$$
$$-C-CH_2-$$
$$\quad |$$
$$\quad C$$
$$\ //\quad \backslash$$
$$O\qquad OH$$
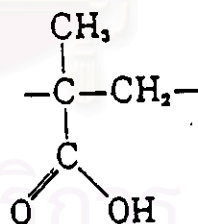
Poly(methylacrylic acid

$$-CH_2-CH_2-O-$$

Poly(ethylene glycol) and poly(ethylene oxide)

$$-CH_2-CH_2-NH-$$

Polyethylenimine

Fig. 2.8 Formulas for some water-soluble binders[10]

Fig. 2.9 Viscosity grade for some water soluble binder [10]

| | Viscosity Grade | | | | | Electro-chemical Type | | | |
	Very Low	Low	Medium	High	Very High	Nonionic	Anionic	Cationic	Biodegradable
Gum arabic	•						X		X
Lignosulfonates	•						X		X
Lignin liquor	•						X		X
Molasses	•					X			X
Dextrins	•——					X			X
Poly(vinylpyrrolidone)	•——					X			
Poly(vinyl alcohol)	•——	—•				X			
Polyethylene oxide			•——•			X			
Starch		•———	——•			X			X
Acrylics		•——•					X		
Polyethylenimine PEI		•———	—•					X	
Methylcellulose			•———	———	—•	X			X
Sodium carboxymethylcellulose			•——	———	—•		X		X
Hydroxypropylmethylcellulose			•———	———	—•	X			X
Hydroxyethylcellulose			•———	———	——•	X			X
Sodium alginate				•——•			X		X
Ammonium alginate				•——•			X		X
Polyacrylamide				•—	—•	X			
Scleroglucan					•	X			X
Irish moss					•		X		X
Xanthan gum					•				X
Cationic galactomanan					•			X	X
Gum tragacanth					•	X			X
Locust bean gum					•	X			X
Gum karaya					•	X			X
Guar gum					•—•		X	X	X

Onoda[11] performed analysis to determine the intrinsic variables which affect the green strength of ideal dry bodies held together by orginic binders. Important parameters are the amount of binder in the body, the strength of the binder and the packing density. As the density of a ceramic increases, the amount of binder by weight required to obtain a given strength decreases. The type of binder used can greatly vary the theoretical strength. Low-molecular-weight binders have low cohesive strengths while high-molecular-weight binders can have higher strength.

Real bodies are generally much more complex because particles are not spheres and are not uniform. The packing density may not be uniform by nonuniform distribution of binder. The properties of organic materials added to spray-dried powders are important to consider and can also affect the spray drying operation.

The interesting character of binders in dry pressing is humidity sensitivity[12], mostly found with long chain polymer (high polymerization) and classified in hydrophilic group, i.e. PVA (polyvinyl alcohol). The binder which has lower T_g (glass transition temperature) can absorb moisture and cause lower yield-point of the granule and effect on pressing properties such as higher green density and compaction, variation in green strength and shrinkage, either increased reject rate or higher machining cost. PEG (polyethylene glycol) usually used as plasticizer blended with PVA in various proportions can change the T_g to be lower and cause the strength reduction and green density increment on granule compaction[13,14].

The amount of binder is typically 0.5 to 4.0 wt% based on the dry weight of the ceramic powder. Excessive amounts will resist deformation of the granules during compaction and cause burnout problems.

2.6 Dry pressing technical ceramics [15,16]

Dry pressing is the uniaxial compaction of loosely granulated dry ceramic powders within a die/punch arrangement. The goals of dry pressing technical ceramics are uniform compact size and green density, consistent part-to-part green density and defect free compact. Production rates vary depending on part geometry and equipment type. Pressing

pressures in the range of 20 to 300 MPa are normally used. Clay based materials commonly used low pressures whereas higher pressure are required for fine technique ceramics. There are three general stages - Die fill, compaction and ejection.

To control the pressed green density of the compact is important to maintain predictable fired density, consistent geometric shrinkage and uniform. The major material variables are agglomerate size, bulk density, compaction ratio of the material, material flow, pressing additives and material compaction under pressure. Spherical particles are preferred and generally produced by spray drying or granulation. High green density prefers broad size distributions. Fine technical ceramic requires agglomerates in the range of 40 to 200 μm while sanitary, refractories or grinding wheels use agglomerates ranging in size from approximately 100 to 1,000 μm (0.1 – 1 mm). The physical nature of agglomerates is significant, both for uniform cavity fill and consistent fill bulk density. An excessive amount of fines leads to poor flow and results in nonuniform die cavity filling. Whereas an excessive coarse fraction may have better flow characteristics but it can lead to a lower bulk density, require higher compaction pressure and lower net fired densities.

The well-controlled bulk density of the powder (fill bulk density) provides a consistent die cavity fill brings to a uniform weight in every compact. Another variable to control of material properties is tapped bulk density that provides some insight to the packing characteristics as the powder settles in the cavity or the feed during a long run of pressing. The difference between the fill bulk density and the tapped bulk density should be minimized. Compaction ratio of the powder, which is the green compact density divided by the fill bulk density, correlates to the

consistency of the properties of the powder through the pressing action. Lukasiewicz [17] developed the compaction model that equated relative changes in green density to relative changes in applied pressure as:

$$D_g = D_f + m \cdot \ln (P_a / P_y) \qquad (2.1)$$

D_g = The compact density at applied pressure

D_f = The fill density of powder

m = The compaction constant

      (depend on packing and deformability of powder)

P_a = The applied pressure

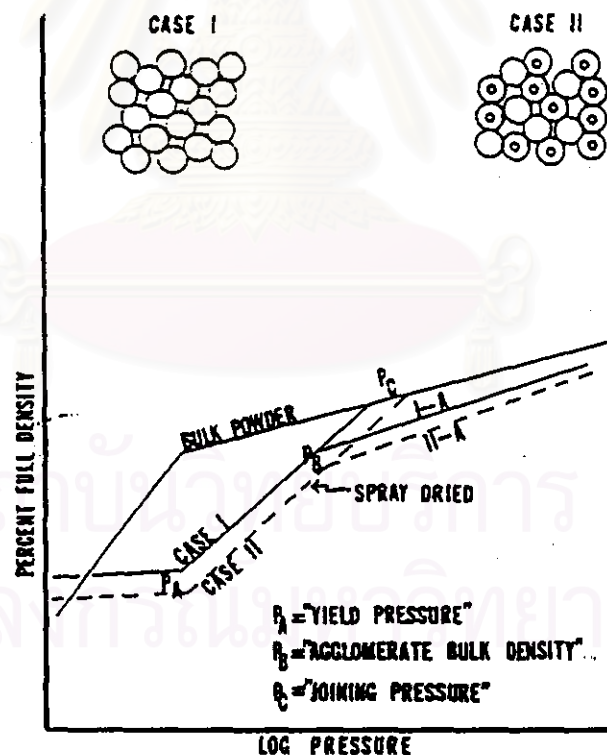P_y = The apparent granule yield pressure

Fig. 2.10 General compaction diagram [17]

From Fig. 2.10, the bulk density of the agglomerates, compaction of the agglomerates may become retarded if the agglomerates resist deformation into interstices (case I-A, II-A). The lower fill density for hollow agglomerates is indicated by case II, the compaction response from P_B (agglomerate bulk density) to P_C (joining pressure) may join curve for case II if hollow agglomerates collapse.

When the agglomerates deform under pressure, interstitial voids usually are the most readily reducible. The minimum required pressure to attain a consistent and high green compact density is optimal because of less wear and reduces potential of damage if properly design of materials. Lower pressure reduces compact defects such as end-capping, finning and delamination.