CHAPTER II

LITERATURE REVIEW

2.1 Rice

Rice, a grass (Gramineae) belonging to the genus *Oryza*, is an annual crop which has monocotyledon and fibrous root system. Although the genus *Oryza* has approximately 20 species, only two species are cultivated, *O. glaberrima* Steud. and *O. sativa* L. While *O. glaberrima* is grown in a few countries in West Africa, *O. sativa* L. is widely cultivated in tropical and subtropical regions (Juliano, 1985a; Grist, 1986; Oka, 1991). *O. sativa* L. is generally classified into three subspecies which are indica type, japonica type and javanica type. However, other criteria to classify the rice subspecies have been proposed; for instance, height of the paddy plant, morphology and length-width ratio of the kernel (Grist, 1986) and variation in isozymes (Oka, 1991).

2.1.1 Gross structure of rice kernel

Structure of mature rice kernel (Fig. 2.1) can be divided into two major parts which are hull and caryopsis. Hull or husk composes of two modified leaves, lemmae and palea, holding together by hooklike structures. The main function of hull is to protect rice caryopsis (Grist, 1986). The second part of the rice kernel is called caryopsis, coated by a film-like layer which consists of pericarp, seed coat and nucellus. Pigments in colored rice are found in pericarp and seed coat layers. The next layer is aleurone layer which completely surrounds rice grain and the outer side of embryo. Thickness of the aleurone layer depends on the position of the layer and the type of cultivars. Embryo or germ is located nearby the base of the rice grain. The embryo is rich in proteins, lipids, vitamins and enzymes. Endosperm of rice kernel is divided into two regions, subaleurone layer and starchy endosperm. The starchy endosperm region is packed with amyloplasts containing large, polygonal, compound starch granules. The amyloplasts are surrounded by protein bodies (Juliano and Bechtel, 1985; Zhou et al., 2002a).

When the hull is removed from paddy, rice caryopsis is obtained and called brown rice or hulled rice. Further milling provides bran and milled rice, or polished rice. While the bran contains pericarp, seed coat, nucellus, aleurone layer and embryo, milled rice contains starchy endosperm. Rice milling causes the loss of proteins, lipids, vitamins, fiber and other minor components from the rice kernel. Therefore, milled rice has lower nutritional values than hulled rice (Juliano and Bechtel, 1985). However, milled rice requires less cooking duration, provides the cooked rice with softer texture and contains available carbohydrate than hulled rice. The relative proportions of hull, bran and milled rice are 20%, 10% and 70% wet basis (wb), respectively (Juliano and Bechtel, 1985, Zhou et al., 2002a).

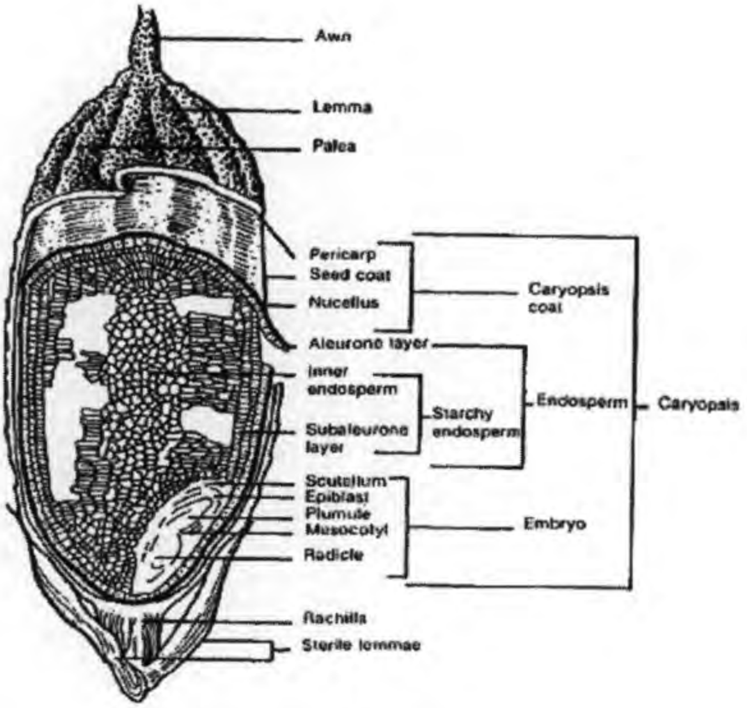

Figure 2.1 Structure of rice grain (Zhou et al. 2002a)

2.1.2 Chemical components of rice

Chemical components of rice caryopsis can be classified into major components and minor components. The rice major components are starch, proteins and lipids which are important to rice qualities (Juliano, 1985b). The minor components include minerals, vitamins, non-protein nitrogen, phenolics and aroma compounds (Juliano and Bechtel, 1985).

2.1.2.1 Major components

a) Starch

Starch is the main component (80-90% wb) in rice grain. The starch granules present as clusters in amyloplasts, filling within the central space of the endosperm (Whistler and Daniel, 1984; Juliano, 1985b; Zhou et al., 2002a). The morphology of rice starch granules is polygonal but irregular in shape (Zhou et al., 2002a). The granules are packed with starch polymers, amylose and amylopectin. Amylose is a slightly branched molecule. It mainly consists of the linear portion of D-glucopyranosyl units linked by $\alpha(1\rightarrow4)$ glycosidic linkage with some $\alpha(1\rightarrow6)$ linkages at branch points (Hood, 1982; Fennema, 1996). Amylopectin is a highly branched molecule consisting of many clusters (Fig. 2.2). Each cluster contains two or three types of $\alpha(1\rightarrow4)$-D-glucan which are A chains, B chains and C chain. The A chains are those which linked to the rest of the molecule by a single $\alpha(1\rightarrow6)$ linkage only through their reducing ends. The B chains are those linked to other A and/or B chains at one or more of their D-glucopyranosyl residues. The C chain is the main chain with the sole reducing end; therefore, only one C chain is found in an amylopectin molecule (Hood, 1982). The average chain length of amylopectin, the frequency of branch points in amylopectin and the relative proportion between amylose and amylopectin varies among rice varieties, resulted in the differences of physicochemical properties and eating qualities among the varieties (Whistler and Daniel, 1984; Juliano, 1985b; Zhou et al., 2002a).

b) Protein

Protein is the second most abundant component in rice grain (Juliano, 1985b; Ju, Hettiarachchy and Rath 2001; Zhou et al., 2002a). The amount of rice protein decreases when milling degree increases (Juliano, 1985b; Zhou et al., 2002a). Protein content in hulled rice and milled rice is approximately 6.6-7.3% dry basis (db) and 6.2-6.9% db, respectively (Juliano, 1985b; Ju, Hettiarachchy and Rath 2001; Zhou et al., 2002a). Rice proteins can be classified into four categories according to their solubility, albumin, globulin, glutelin and prolamin which can be soluble in water, salt solution

(0.4 M NaCl), dilute acid and alkali, and alcohol (70-80% ethanol), respectively. The main protein in rice is glutelin, specifically called oryzenin (Juliano, 1985b; Chrastil, 1990; Chrastil and Zarins, 1992; Ju, Hettiarachchy and Rath 2001; Zhou et al., 2002a). The relative proportions of albumin, globulin, glutelin and prolamin in hulled rice are approximately 5%, 12%, 80% and 3%, respectively (Ju, Hettiarachchy and Rath 2001). Protein is most abundant in subaleurone layers. Albumin and globulin are mainly located in the outer layers of rice kernel. In endosperm, two main forms of rice protein are found. The first one is large spherical protein bodies which are rich in prolamin. The other is crystalline protein bodies which are rich in glutelin (Juliano, 1985b; Zhou et al., 2002a).

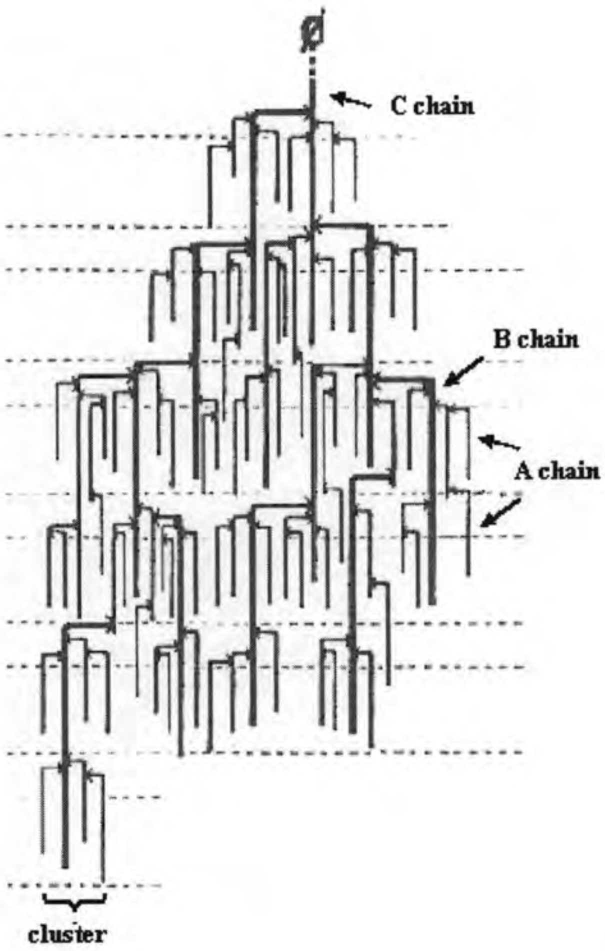

Figure 2.2 Structure of amylopectin (Hood, 1982). The symbol "ϕ" represents reducing end of the molecule.

c) Lipid

Most of lipids in rice grain are located in the outer layers. In aleurone layer and embryo, rice lipids are formed as lipid droplets or spherosomes, while, within endosperm, lipids are associated with protein bodies and starch granules. The lipids content in hulled rice and milled rice is approximately 1-4% wb and 0.2-2.0% wb, respectively (Juliano, 1985b; Zhou et al., 2002a). Rice lipids consist of triglycerides, free fatty acids, glycolipids and phospholipids. The main fatty acids in rice grain are linoleic (C18:2), oleic (C18:1) and palmitic (C16:0) acids. The minor fatty acids are myristic (C14:0), stearic (C18:0), linolenic (C18:3), lauric (C12:0) and arachidonic (C20:4) acids (Juliano, 1985b). Rice lipids can also be classified as non-starch lipids and starch lipids. The non-starch lipids are distributed throughout the rice grains but concentrated in rice bran. The starch lipids are associated with starch granules (Juliano, 1985b; Morrision, 1995; Zhou et al., 2002a). Some of the starch lipids may form inclusion complex with amylose; therefore, they can affect physicochemical properties of starch, such as retarding the swelling of the starch granules (Juliano, 1985b; Zhou et al., 2002a). The content of the starch lipids is directly proportional to the backbone of amylose content in rice starch (Morrision, 1995).

2.1.2.2 Minor components

a) Aroma compound: 2-acetyl-1-pyrroline (2AP)

The characteristic of cooked rice flavor is related with numbers of volatile compounds and their threshold (Buttery, Turnbaugh and Ling, 1988). The 2AP (Fig. 2.3) has been identified as a key component providing desirable flavor in cooked rice (Buttery, Ling and Mon, 1986; Buttery et al., 1988; Wongpornchai, Sriseadka and Choonvisase, 2003). The amount of 2AP in rice grain depends on the varieties of rice and cultivated conditions (Yoshihashi, Huong and Inatomi, 2002). The content of 2AP in rice grain is lower than 0.006 to 0.008 ppm but fragrant rice contains approximately 0.04-0.09 ppm. Since the content of 2AP in rice is low, it easily diffuses out of rice grain. The odor threshold of 2AP is 0.0001 ppm in water (Buttery et al., 1983).

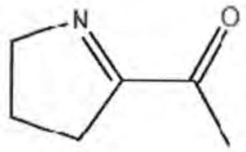

Figure 2.3 Chemical formula of 2-acetyl-1-pyrroline (Hofmann and Schieberie, 1998)

The 2AP is synthesized at aerial parts of rice plants during growing in the fields (Yoshihashi, 2002). Although the pathway of 2AP synthesis is still vague, the possible pathway (Fig. 2.4) was proposed by Yoshihashi et al. (2002). The authors suggested that L-proline was the precursor in 2AP synthesis in aromatic rice as a nitrogen source. However, L-proline was not the carbon source of acetyl group in 2AP.

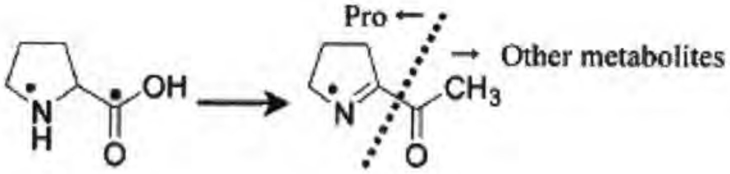

Figure 2.4 Possible pathway of 2-acetyl-1-pyrroline in aromatic rice
(Yoshihashi et al., 2002)

KDML-105 is a well-known cultivar of Thai fragrant rice. It has been widely used as a model for the analysis of aroma compounds, especially 2AP. Mahatheeranont, Keawsa-ard and Dumri (2001) compared the two different methods of extraction of the aroma compounds in uncooked hulled KDML-105 rice. The first method involved indirect steam distillation and solvent extraction using dichloromethane. In the second method, only solvent extraction was employed. The aroma compounds in the extracted solvent were then analyzed using gas chromatography-mass spectrometry (GC-MS). In the first method, more than 140 volatile compounds were shown in the chromatogram whereas, in the second method, less complicated chromatogram was reported. As a result, quantitative analysis of the aroma compounds using peak area of the chromatogram from the solvent extraction was more efficient. Therefore, the solvent extraction technique was proposed to be a convenient, inexpensive and efficient way to extract and quantify rice aroma compounds. In this procedure, the samples were not exposed to high temperature during extraction. Thus, the degradation of 2AP could be minimized. The amount of 2AP in the uncooked brown rice was reported as approximately 0.34 ppm. Hexanal, nonanal, butyl acetate and diethyl carbonate were also identified. Sunthonvit, Srzednicki and Craske (2003) analyzed the volatile components in KDML-105 rice using modified Likens and Nickerson apparatus and GC-MS. Various types of volatile compounds were found, including aldehydes, alcohols, ketones, heterocyclic hydrocarbon and acids. The content of 2AP in KMDL-105 rice reported in this study was 44.7 ppb. Sriseadka, Wongpornchai and Kitsawatpaiboon (2006) developed methods to analyze 2AP in rice grain using static headspace gas chromatography (HS-GC) equipped with Flame ionization detector (FID) or nitrogen-phosphorous detector (NPD). The authors indicated that the developed technique provided higher sensitivity and precision than the solvent extraction technique. The limits of detection of HS-GC-FID and HS-GC-NPD were 20 ng and 5 ng of 2AP, respectively. The HS-GC method was also less time-consuming and solvent-free. The authors also reported the amount of 2AP in KMDL-105 rice in hulled and milled rice using the developed HS-GC-FID. The results showed that the amount of 2AP in the hulled rice was 3.83 ppm while in the milled rice was 2.37 ppm. Another solvent-elimination technique which had been employed to study 2AP in rice is solid-phase microextraction (SPME). Working conditions and efficiency of SPME were reported in several researches (Grimm et al., 2001; Wongpornchai et al., 2004; Gay, et al., 2006; Tulyathan, Srisupattarawanich and Suwanagul, 2008).

2AP was also considered as a flavor characteristic compound in pandan leave (*Pandanus amaryllifolius* Roxb) (Maga, 1984; Yoshihashi et al., 2002), pecan (Maga, 1984), popcorn (Schieberle, 1991; Yoshihashi et al., 2002), bread flowers (*Vallaris glabra* Kize) (Wongpornchai et al., 2003), cured ham and roasted beef (Carrapiso et al., 2002).

2.1.3 Red jasmine rice

"Red jasmine rice" or "Khao Hom Ma Li Dang" (*Oryza sativa* L.) is one of the Thai fragrant rice cultivars, naturally mutated from Khao Dawk Mali 105 (KDML-105). Hulled red jasmine rice has red pericarp which contains high level of phenolic antioxidants (Suttajit, 1999). The origin of red jasmine rice is still ambiguous. Supanburi province and Surin province have been proposed as the origin of red jasmine rice. Red jasmine rice is now cultivated in some central, western and northeastern provinces in Thailand. The proper cultivating season is rainy season, from August to November. The average tiller number is 192 per square meter. The height of rice plant is approximately 120-130 cm. Red jasmine rice has low amount of chalky kernels. The hulled rice has low amylose content. Cooked red jasmine rice provides soft texture and unique aroma comparing to those of KDML-105 (Rice Research Institute, 2006).

2.2 Organic farming

Organic farming is a type of agriculture which prohibits the application of agrochemical substances, including synthetic fertilizers, pesticides, herbicides, plant growth regulators and livestock feed additives. Genetically modified organisms (GMOs) are forbidden in organic farming as well. Soil productivity and pest control are usually done by crop rotation, utilization of green manure and crop residue. The methods of organic farming are based on the standards set by International Federation of Organic Agriculture Movements (IFOAM). However, the farmers can set their own systems due to different criteria, such as climate, market conditions, and agricultural regulations in each country. In most countries, organic farming must be accredited by the authorized agencies. Organic certification is also required for the import and export of organic produces. Nowadays, organic farming and organic products can contribute to ecologically sustainable development. Market size for organic products has been increasing in both local and international levels (Paull, 2006).

2.3 Effects of postharvest handling on physicochemical properties of rice

2.3.1 Determination of physicochemical properties of rice flour

2.3.1.1 Thermal properties

Thermal properties of rice flour are usually determined by differential scanning calorimeter (DSC). Power-compensation DSC (Fig. 2.5) has widely been used to determine thermal behavior of rice flour (Zobel, 1984). Temperatures of the sample and reference in power-compensate DSC are controlled independently by individual heaters. When the sample pan and the reference pan are heated, any types of thermal transition could occur. The samples may absorb or release heat, leading to temperature difference between samples and reference. The instrument will provide heat to flow into or out of samples to a maintain temperature balance as previously set in the controlled temperature program. DSC then records the difference in heat flow between the sample and reference as a function of time or temperature. If the reference pan is empty, the heat flow difference will represent the transition energy in the sample (Reid et al., 1993; Reid, 2002). DSC result is shown as a DSC thermogram (Fig 2.6). An increase in heat flow during heating represents endothermic process during gelatinization of any starchy materials, including rice flour (Zobel, 1984). The DSC parameters, including onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c) and enthalpy of gelatinization (ΔH_g) calculated from the area under peak are automatically reported by the instrument.

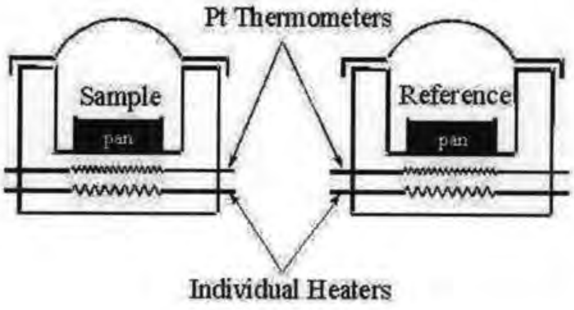

Figure 2.5 Schematic diagrams of power-compensate and DSC (Bhadeshia, 2007)

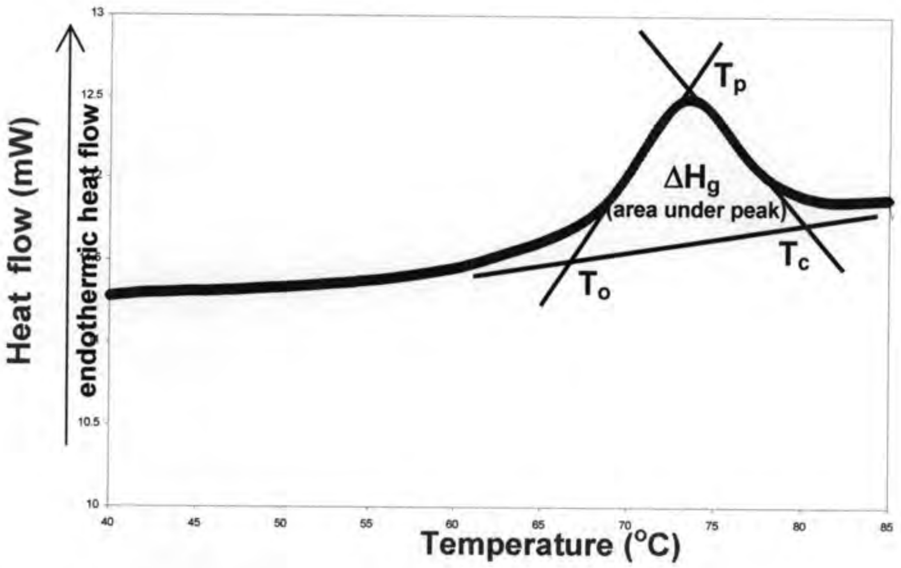

Figure 2.6 A DSC thermogram

DSC has been used to analyze thermal transitions of many starch-based products and cereal components (Eliasson, 2003). For example, as for bread, T_o can indicate the temperature when changes in starch component in dough begin. At higher temperature, an increase in viscosity was attributed to starch gelatinization. Since starch gelatinization and crumb fixation can stop volume expansion of crumb, if T_o is high, there will be a longer period of time for volume expansion to occur (Eliasson, 2003).

2.3.1.2 Pasting properties

The Rapid Visco Analyzer (RVA) is commonly used to analyze pasting behaviour of starch and flour samples during heating and cooling cycle in an excess water condition. In the heating cycle, starch slurry will be heated from 50°C to 95°C with stirring. As temperature increases, intermolecular hydrogen bonds of starch molecules are disrupted. This change results in an increase in free hydroxyl groups, which can bind with water molecules by hydrogen bonding. As a result, the starch granule can absorb more water and further swell, leading to an increase in the viscosity. At a critical temperature, the viscosity of the paste will dramatically increase. That temperature is called pasting temperature (PT). While the starch granules had the maximum swelling, starch paste will have maximum viscosity, called peak viscosity (PV).

When the temperature of the starch paste reached 95°C, the paste is held at 95°C with continuously stirring. In this situation, highly swollen starch granules are easily disintegrated by shear force, leading to a decrease in paste viscosity. Minimum viscosity during heating process is called trough (T). The difference between PV and T is represented as breakdown (BD) which corresponds with the ability of the starch granules to rupture. After that, the paste will be cooled to 50°C. Amylose molecules which leach from damaged starch granules can rearrange and interact with each other (retrogradation), resulted in an increase in paste viscosity. Viscosity at the end of RVA run is called final viscosity (FV). The difference between FV and T is represented as setback (SB). (Fennema, 1996; Zhou et al., 2003).The results are shown as RVA curve (Fig. 2.7). RVA parameters are automatically reported by the instrument.

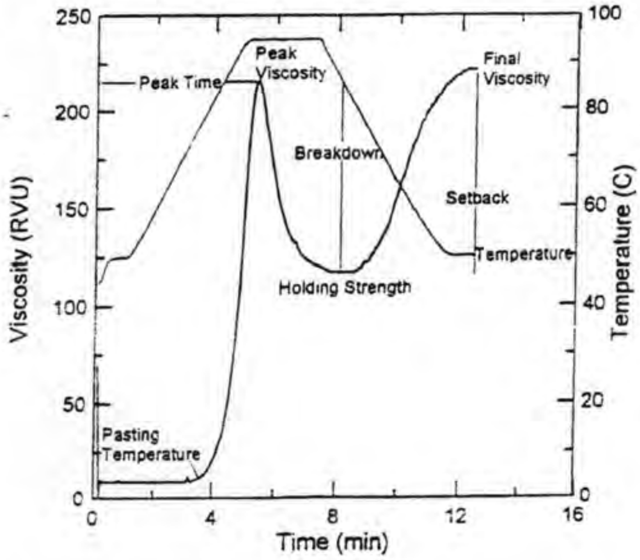

Figure 2.7 RVA curve (Zhou et al., 1998)

RVA has become popular for starch analysis as this instrument consumes less time and fewer amounts of samples than traditional techniques. Data from this instrument has been applied for selection of suitable starches in many food products, including can foods, dressings, and soups. For instance, starch used as a thickener in can food products should have low PT and SB, but have high PV, as it should easily gelatinize prior to retort process and provide high viscosity. Adequate viscosity during filling step can help keeping food particles homogeneously suspended and prevent splattering of the product. Moreover, starch should breakdown to watery consistency during retort process in order to prevent gelation in a can which may provide undesirable characteristics of some retorted products, including canned soup (Thomas and Atwell, 1999).

2.3.2 Effects of paddy drying methods on physicochemical properties of rice

Moisture content of fresh paddy is 26-30% wb. This level of moisture content is suitable for the growth of insects and microorganism, leading to the deterioration of paddy. Therefore, the reduction of moisture content of paddy is essential (Brooker Brooker, Bakker-arkema and Hall, 1975; Grist, 1986). There are several methods to reduce moisture content of paddy, including shade drying, sun drying and fluidized bed drying.

a) Shade drying

Shade drying is a simple method. Paddy is dried by air at ambient temperature in shade area until its moisture content reaches desirable level. The advantage of this method is an inexpensive cost. However, it requires long period of drying which is 5-7 days. The quality of rice is inconsistent. This method is applied as a control method in many studies which investigate effects of drying conditions on qualities of rice (Rarisara Impaprasert, 2549).

b) Sun drying

Sun drying is the common drying method used to dry agricultural products in the most tropical countries. As for paddy, it is spread on a concrete, a mat, or in a field and naturally dried under sunlight. The production cost and quality of paddy from this method are similar to those obtained from shade drying but the drying time can be reduced to 1-2 days. This method is generally used by most farmers (Imoudu and Olufayo, 2000).

c) Fluidized bed drying

Fluidized bed (FB) drying (Fig. 2.8 and Fig. 2.9) has been introduced to commercial paddy drying in Thailand (Soponronnarit, 1999). It can faster reduce moisture content of fresh paddy and provide the dried paddy with more uniform qualities than the traditional shade drying and sun drying. The principle of the FB drying is to apply hot air to solid particles which will behave like fluid. In a batch FB dryer, flow direction of air and solid particles is usually opposite (counter flow) (Fig.2.9). Consequently, the rapid transfer of heat and moisture between solids and air was occurred due to the large contact surface area between raw materials and hot air. Therefore, the drying time was shortened. However, its operating and maintenance cost is expensive (Daud 2005).

Figure 2.8 A batch hot air fluidized bed dryer

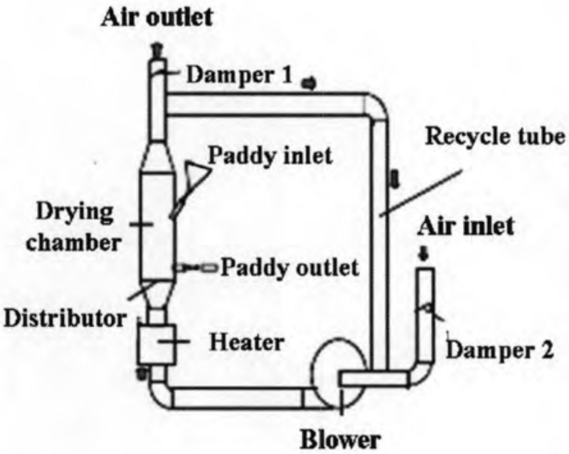

Figure 2.9 A schematic diagram of batch hot air fluidized bed dryer (Rordprapat et al., 2005)

Previous studies indicated that the different drying methods affected physicochemical properties of rice. Tirawanichakul et al. (2004) examined the effects of paddy drying temperature used in FB dryer and initial moisture content of the paddy on the qualities of milled rice. Two rice cultivars, Suphanburi 1 and Pathumthani 1, were dried by 2-stage drying. The paddy was FB-dried in the first stage and tempering for 30 minutes to reduce moisture content of the paddy to 18% wb. The drying temperature was varied from 40°C to 150°C with 10°C increments. The samples were then shade-dried at ambient temperature until the final moisture content of the paddy was 13-14% wb. The control samples were only shade-dried. Thermal properties of samples were analyzed using DSC. The DSC results showed that the samples dried at 150°C had lower ΔH_g than that of the control samples. Wiset et al. (2003) investigated the effects of FB drying temperature on pasting properties of milled rice. The Langi, Amaroo and Chainart paddy with 27% moisture content (wb) was dried by FB dryer at 100°C, 125°C and 150°C to reduce the moisture content to 19-20% wb. The paddy was then shade dried at ambient temperature until the final moisture content reached 13% wb. Pasting properties of the milled rice were analyzed using RVA. The results indicated that an increase in drying temperature led to an increase in PT and SB while PV and BD decreased. Borompichaichartkul et al. (2005) studied the effects of paddy drying temperatures on pasting properties of Thai rice cultivar, KDML-105. The samples were dried by FB dryer at 115°C, 125°C, 135°C and 150°C, tempering for 30 minutes, and finally dried by FB dryer at the same temperature as used in the first step. The results from this study corresponded with the study of Wiset et al. (2003) which pointed out that when paddy drying temperature increased, PT and SB increased, whereas PV, BD and T decreased.

Several studies have shown that paddy drying temperature also affected the structure of some chemical components in rice grains. Inprasit and Noomhorm (2001) investigated the effects of paddy drying temperature and grain temperature on rice quality. The samples of two rice cultivars, KDML-105 and Suphanburi 1, were dried by shade drying, sun drying, oven drying (45°C and 60°C) and FB drying. FB drying was divided into 2 stages. In the first stage, the samples were dried in FB dryer at 120°C for

1.25 minutes. The samples were then tempering for 2 hours and shade dried at ambient temperature (26-35°C). Microstructure of the dried kernels from each drying methods was investigated using scanning electron microscopy (SEM). SEM images showed that the starch granules of FB-dried samples had less polygonal boundaries than shade-dried and sun-dried samples. The authors proposed that these morphological changes could result from the partial gelatinization/melting of starch granules in the samples dried in FB dryer. Tang et al. (2002) studied the effects of drying conditions, including tempering, on the changes of oryzenin. The fresh paddy, cv. Cypress, was initially dried at 60°C until the 4% or 5% (wb) moisture content was removed from the paddy. Some portions of paddy from each treatment were tempered at 60°C for 3 hours. The control samples were dried at 25°C without tempering. Subsequently, all samples were shade-dried at 21°C, 50% RH for 2 days. The final moisture content of the dried paddy was approximately 12.5% wb. The oryzenin was extracted from rice flour and its surface hydrophobicity was investigated. The results indicated that oryzenin extracted from the paddy dried at 60°C had the higher surface hydrophobicity than that of the control samples. Tempering insignificantly affected surface hydrophobicity of the samples ($p>0.05$). Since surface hydrophobicity could indicate denaturation of protein due to an unfolding of protein molecules and an exposure of hydrophobic group, it could be pointed out that the denaturation of oryzenin in fresh paddy occurred during this drying treatment. The corresponding results were also shown by Ju et al. (2001). The authors reported that surface hydrophobicity of 1% oryzenin solution, dissolved in 0.01 M phosphate buffer, remarkably increased when the solution was directly heated in water bath at 65-95°C for 10 minutes.

The difference of paddy drying methods also affected aroma compounds in rice grain. Sunthonvit et al. (2003) investigated the effects of paddy drying temperature on flavor components of KDML-105 rice. The paddy was dried by two-stage drying. In the first stage, paddy was FB-dried at 100°C, 125°C or 150°C to reduce moisture content from 26% wb to 18% wb. The FB-dried paddy was then shade dried at ambient temperature until the final moisture content reached 13-14% wb. Volatile compounds were extracted from milled rice using a modified Likens and Nickerson apparatus and analyzed using GC-MS. The results showed that when paddy drying temperature increased, hexanal increased. Hexanal has been defined as a key compound providing off-flavor in rice grain (Sowbhagya and Bhattacharya, 1976). Wongpornchai et al. (2004) studied the effects of paddy drying methods on aroma of KDML-105 rice. The samples were dried in modified air at 30°C and 40°C, in hot air at 40°C, 50°C, and 70°C and sun-dried until the moisture contents were reduced from 28% wb to 13–15% wb. The dried paddy was kept in gunnysacks and stored at 20–35°C and 70–85% RH for 4 weeks. The paddy was then dehusked by hand and ground to obtain rice flour. The volatile compounds were extracted and measured using SPME-GC-MS. The contents of volatile compounds were shown as the ratios between peak area of the compounds and those of internal standard, 2,4,6-trimethylpyrridine (TMP). The results indicated that the samples dried at low temperature had the higher amount of 2AP but lower amount of n-hexanal than those dried at high temperature. The results of n-hexanal from this research were consistent with those in the studies of Sunthonvit et al. (2003) while the deteriorated effect of elevated drying temperature on 2AP content has also been reported by Borompichaichartkul et al. (2005).

2.3.3 Effects of storage conditions on physicochemical properties of rice

In accordance with earlier studies, storage conditions affected physicochemical properties of rice. Zhou et al. (2003) kept milled rice, cv. Kyeema, Koshihikari and Doongara, in air-tight bottle and stored at 4°C or 37°C for 16 months. Thermal properties of the stored samples were analyzed using DSC. The results indicated that an increase in storage temperature resulted in an increase in T_p and ΔT_g. Pasting properties of the samples were also investigated using RVA. The results showed that for the samples stored at 4°C, PV and BD of the samples increased during 16-month storage. Conversely, for the samples stored at 37°C, PV and BD decreased during the storage. In the study of Sowbhagya and Bhattacharya (2001), fifteen cultivars of paddy were selected based on their contents of amylose equivalent to investigate the effects of aging on their pasting properties. The paddy was placed in metal containers at 26±6°C for 4 years. The pasting properties of milled rice were examined using

Brabender viscoamylograph. The results indicated that an increase in storage duration led to a decrease in BD while SB increased. Pearce et al. (2001) investigated the effects of drying temperature and storage conditions on milling, cooking and pasting properties of milled rice. The authors packed paddy, cv. Cypress, Kaybonned and Bengal, in zipper-sealed plastic bags and then stored in air tight buckets at 4°C, 21°C or 38°C for 4 months. The results showed that PV of the samples increased during 4-month storage. The change with a greater extent in PV could be observed when the samples were stored at higher temperature. Wiset et al. (2003) studied the effects of paddy storage on pasting properties of rice. The authors stored paddy, cv. Langi, Amaroo and Chainart, at 25°C for 4 months. The RVA results indicated that PV and SB of the samples increased during 4-month storage. Tulyathan and Leeharatanaluk (2007) kept milled KDML-105 rice in polypropylene (PP) bags, with 60-μm thickness, and stored at ambient temperature (30-35°C) for 8 months. Pasting properties of the samples were investigated using RVA. The RVA results showed that PV and BD continuously decreased during the 8-month storage. Soponronnarit et al. (2008) stored milled rice, cv. KDML-105, in plastic bags at ambient temperature for 6 months and investigated pasting properties using RVA. The results indicated that PV initially increased in the first 2 months of the storage, then decreased. Conversely, PT, SB and FV increased during 6-month storage.

From this literature review, the time-dependent changes of the pasting properties of the rice flour can be summarized as follows. In the early stage of storage, approximately 2 or 4 months, at ambient temperature or higher, PV of the rice flour may increase, and then decrease afterwards. However, the elevation of PV in the early stage of storage may not be found as reported in the study of Tulyathan and Leeharatanaluk (2007). In case of BD and SB, BD decreases while SB increases during a long-term storage.

Although the quantitative changes of starch, proteins and lipids were minimal (Juliano, 1985c; Chrastil, 1990; Zhou et al., 2002b; Tulyathan and Leeharatanaluk, 2007), numerous qualitative changes of the chemical components in rice grain could occur during storage. The latter changes have been suggested as a cause of the time-dependent changes in physicochemical properties of rice during storage. According to the earliest hypothesis of Moritaka and Yasumatsu (1972) (Fig 2.10), chemical reaction of lipids could greatly affect physicochemical properties of rice during storage. Lipids could be hydrolyzed by lipase, yielding free fatty acid which can form a complex with amylose. The free fatty acid-amylose complex could retard the swelling of starch granules and eventually affected the texture of cooked rice. Alternatively, lipids could undergo auto-oxidation yielding hydroperoxide and carbonyl compounds. These compounds were recognized as the precursors of off-flavor compounds in cooked rice. Hydroperoxide and carbonyl compounds could accelerate the formation of the disulfide bridge (-S-S-) in proteins which affected texture and aroma of cooked rice as well. However, Sowbhagya and Bhattacharya (2001) pointed out two arguments on the roles of lipids in this hypothesis. The first argument involves the changes of the physicochemical properties of waxy rice during storage. As waxy rice had low amylose content, the contents of amylose-lipid complex formed in waxy rice during storage could be lower than those in non-waxy rice. Therefore, as for the hypothesis of Moritaka and Yasumatsu (1972), minor changes in the texture of cooked waxy rice after storage should have been found. However, according to the study of Sowbhagya and Bhattacharya (2001), the changes of physicochemical properties and texture of waxy rice during storage was comparable to those changes of non-waxy rice. In the second argument, Sowbhagya and Bhattacharya (2001) cited the study of Unnikrishnan and Bhattacharya (1995) which indicated that stored parboiled rice had the similar changes of physicochemical properties as stored raw rice. During the processing of parboiled rice, the rice grains were exposed to high temperature, leading to the denaturation of lipase and other enzymes. Without lipase activity, the lipids could not undergo hydrolysis during storage; thus, textural changes of parboiled rice should have been retarded. However, the results of the study of Unnikrishnan and Bhattacharya (1995) were not corresponded to the hypothesis of Moritaka and Yasumatsu (1972). Therefore, these two arguments pointed out that the lipid hydrolysis resulted from lipase activity and amylose-lipid complex formation during storage might not be the important pathways affecting the changes of the physicochemical properties of aging rice.

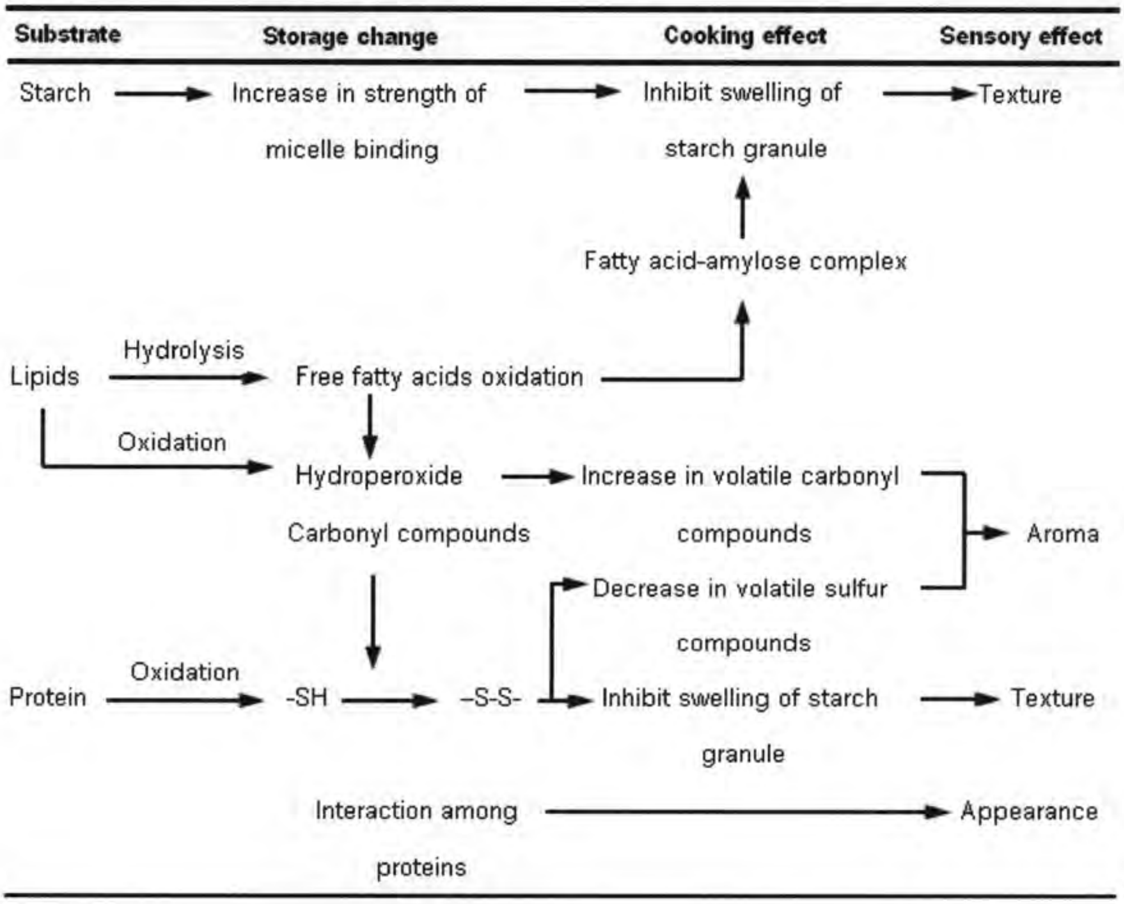

Figure 2.10 A Schematic of mechanism of chemical changes during storage of rice grain (Moritaka and Yasumatsu, 1972)

From Fig. 2.10, other than lipids and starch, proteins could play an important role in the physicochemical changes of rice during storage. Many following studies have supported this suggestion. Chrastil (1990) stored milled rice in closed jar at 4°C and 40°C for 12 months. The oryzenin was extracted from the samples and its solubility, average molecular weight, measured from intrinsic viscosity and ultracentrifugation, as well as the amount of sulfhydryl group and disulfide bridge were investigated. The results showed that the rice samples stored at 40°C for 12 months had the extracted oryzenin with lower solubility, higher average molecular weight, containing lower amount of sulfhydryl group and higher amount of disulfide bridge comparing to those of fresh rice samples. Chrastil and Zarins (1992) stored milled rice at 40°C for 12 months. Oryzenin was extracted from the samples and its electrophoretic pattern was investigated using SDS-PAGE at 15°C and Coomassie Brilliant Blue R-250 was used as dye-stain. The results showed that low molecular weight peptides (14200, 22000-23000, 32000-37000 and 56000 Dalton) decreased while high molecular weight peptides (79200, 83000, 91300, 104000 and 202000 Dalton) increased during storage. The results in these two studies was corresponded with the hypothesis of Moritaka and Yasumatsu (1972) that the sulfhydryl group of oryzenin was oxidized to form disulfide bridges during storage of rice kernels, resulting in an increase in average molecular weight of oryzenin. The structural change of oryzenin has been shown to affect physicochemical properties of rice. Martin and Fitzgerald (2002) studied pasting properties of fresh milled basmati rice and the samples stored at 4°C. Some stored samples were treated with Tricine-dithiothreitol (Tricine-DTT) buffer in order to disrupt disulfide bridges. Pasting properties of rice flour were then measured by an RVA. The results showed that stored samples treated with Tricine-DTT provided the similar RVA curves as those obtained from the fresh samples. Corresponding results also obtained from the study of Zhou et al. (2003) who observed the RVA results of the stored rice flour treated with β-mercaptoethanol, which is another type of reducing agent. An increase in disulfide bridge of oryzenin during storage could restrains starch swelling during the heating process, resulted in the changes of physicochemical properties of rice flour. Apart from oryzenin, other groups of proteins might also involve in the changes of physicochemical properties of aging rice. For instance, the initial rise of PV in the early stage of storage has also been proposed as the effect from the decline of the activity of α-amylase within rice samples during storage (Sowbhagya and Bhattacharya, 2001; Zhou et al., 2002b).

Aroma compounds of rice can also change during storage. Wongpornchai et al. (2004) investigated the effects of storage conditions on the flavor compounds in KDML-105 rice. The dried paddy was kept in gunnysacks and stored at ambient conditions (20–35°C) with 70–85% RH for 10 months. The flavor compounds in the hulled rice were examined using SPME-GC-MS. The results indicated that the amount of 2AP decreased while n-hexanal increased during storage. Yoshihashi et al. (2005) studied the effects of storage conditions, including packaging materials and storage temperature, on 2AP in KDML-105 rice. The milled rice was kept in linear density polyethylene (LDPE) bags or nylon mesh bags and then stored at 5°C, 20°C, 25°C or 30°C for 10 weeks. The 2AP was extracted by ethanol and analyzed using GC-MS. The results from this study indicated the loss of 2AP during storage. The higher storage temperature, the greater decline of the amount of 2AP in rice grains was observed. Although the content of 2AP in the samples stored in LDPE bags decreased slower than those stored in nylon mesh bags, the authors proposed that LDPE bags were still not the most suitable packaging materials for storage of fragrant rice. As for the study of Rarisara Impaprasert (2549), the KDML-105 paddy was dried by FB dryer, packed in gunny sacks and stored at ambient temperature (28-30°C) or 15°C for 6 months. The contents of 2AP were examined using HS-GC. The results from this study showed the decrease in 2AP content during storage. The samples stored at high temperature showed greater decrease in the amount of 2AP. Tulyathan and Leeharatanaluk (2007) studied the effects of storage duration on the content of 2AP in KDML-105 rice as well. Hulled KDML-105 rice was kept in PP bags, with 60-μm thickness, and stored at ambient temperature for 8 months. The 2AP was extracted from stored milled rice by acidic solution and examined using GC-FID. The contents of 2AP were presented as the ratios between peak area of 2AP and those of TMP. The results showed that, in the first 3 months of the storage, the amount of 2AP remarkably decreased and remained only 18% of the original content in the fresh hulled rice. The 2AP then gradually decreased afterwards. Tulyathan et al. (2008) studied the effects of storage conditions on the volatile compounds in hulled rice, cultivar Jao Hom Supanburi. The samples were packed in PP, with 30-μm thickness, or vacuum-packed in laminated oriented polypropylene/aluminum/linear low density polyethylene (OPP/AL/LLDPE) bags and stored at ambient temperature (27-32°C) for 6 months. The volatile compounds were extracted from the samples and measured using SPME-GC-MS. TMP was used as an internal standard. The authors reported the contents of 2AP as the ratios of peak area between 2AP and TMP. The results revealed that the content of 2AP decreased whereas n-hexanal increased during storage. The average contents of 2AP in the samples stored for 6 months and packed in PP and laminated OPP/AL/LLDPE bags were 41% and 57% of the 2AP amounts in the fresh rice, respectively. The authors indicated that the laminated OPP/AL/LLDPE film is a better barrier than PP film. Therefore, the laminated OPP/AL/LLDPE bags could prevent the loss of the 2AP and the diffusion of oxygen into the bags. As a consequence, lipid oxidation could be retarded, resulted in the low n-hexanal content.

As for the above literature review, the effects of storage temperature and storage duration on the amount of 2AP and n-hexanal from different studies are consistent. When storage duration increases, the amount of 2AP decreases while n-hexanal increases. The higher storage temperature, the faster deterioration of the 2AP and the faster formation of n-hexanal in rice occurs. Using proper packaging materials can preserve desirable aroma and prevent the off-flavor formation in hulled and milled rice. According to this review, laminated OPP/AL/LLDPE bag is the most suitable packaging to prevent the loss of 2AP and retard the formation of off-flavor compounds in rice during storage.