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Review

The ageing mechanism of stored rice: A concept model from the past to the present

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A B S T R A C T

Rice ageing is a complicated process. Ageing is unique in rice: no other grains show such behaviors. More recent years, novel techniques, such as HS-SPME–GC–MS and e-nose system were used to monitor rice ageing process. Storage conditions were also investigated for minimizing rice ageing process, and the literature indicated hermetic storage could significantly improve overall paddy quality, with providing a more practical and useful method for maintaining rice quality and controlling insect mortality during rice storage. Although there were no significant differences in the gross contents of starch, cell wall remnants, proteins and lipids, the ageing process did cause a shift in the components of a number of chemical groupings. Studies also showed that the interactions among macro- and micro-compositions in rice grains during storage would play key roles on the changes of rice overall physicochemical and cooking properties. Based on recent years' studies, a conceptual model for interpreting rice ageing mechanism is proposed.

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1. Introduction

Rice (*Oryza sativa* L.) is one of the most widely cultivated cereals around the world. It is a typical staple food consumed by nearly half the world's population, in particular for Asian, South-American and African countries. Although a small amount of the rice crop is processed to be used as food ingredients and feed constitutes, the bulk is consumed as cooked rice (Zhou et al., 2002a). This pattern of usage results in the need to store rice over varying periods. During storage, a number of changes in rice physicochemical and cooking properties occur, which is usually termed rice ageing (Zhou et al., 2002a). Compared to fresh rice, the aged rice demonstrated different properties, which included chemical composition, physicochemical property (Park et al., 2012), sensory evaluation (Kaminski et al., 2013; Griglione et al., 2015; Sung et al., 2014),

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cooking property (Zhou et al., 2007a) and even hygienic issues (Choi et al., 2015). Consumers in south Asia dislike new rice but those in northeast Asia dislike aged rice. Further research indicates that these parameters are correlated well with each other. For example, white rice stored at a low temperature retained its white coloration, whereas low color retention values were obtained at higher storage temperatures (Park et al., 2012), which was related to a greater fat acidity (Sung et al., 2014) and the oxidation of the lipids (Tulyathan et al., 2008) during the storage. The understanding of rice ageing mechanism would provide valuable information to rice processing industries for correlating the ageing conditions with the processing functionalities of different rice varieties.

2. Effect of specific storage conditions on rice quality

Hermetic storage of rice seems to be more practical and useful methods to maintain rice quality and control insect mortality during storage. It was proposed that the use of hermetic storage led to a safe, pesticide-free, and sustainable storage method, suitable for rice seeds (Guenha et al., 2014). Consistent result was also achieved from the study of RohithaPrasantha et al. (2014) by comparing the paddy storage either in hermetic IRRI bags or common woven polyethylene bags at room temperature for 9 months, and they found that hermetic storage of dry paddy could significantly improve overall paddy quality, including insect mortality, gas contents, moisture content, thousand grain mass, porosity, hardness, whiteness, total milled rice yield, head rice yield, gelatinization temperature, amylose, crude protein, crude fat, free fatty acid (FFA), and sensory characteristics. More recently, radio frequency technology was also developed for postharvest insect control in milled rice (Zhou et al., 2015).

3. Effect of ageing process on rice chemical compositions

Starch is generally considered an inert ingredient; thus, the change of starch content in rice is believed to be insignificant over time during rice ageing. Rehman (2006) and Cao et al. (2004) observed a slight increase of reducing sugar content in aged rice, indicating the enzymatic degradation of starch might occur during storage. In addition, as rice aged, an increase in the percentage of short chains (DP 6–12) was also reported by Patindol et al. (2005). Huang and Lai (2014) studied the effects of endogenous amylase on the starch fine structure and its relationship to the pasting property of the aged waxy rice and found that the state of the starch fine structure changed and exhibited a decreasing percentage of longer chains but an increasing percentage of shorter chains of amylopectin when the rice was stored at a higher storage temperature for a longer duration.

The studies of rice other chemical compositions suggested that although there were no significant differences in the gross contents of starch, cell wall remnants, proteins and lipids, the ageing process did cause a shift in the components of a number of chemical groupings (Zhou et al., 2002a). For example, the amount of storage proteins (i.e., prolamins and glutelins) in the propanol-extractable fractions decreased for aged rice compared to its corresponding fresh rice (Zhou et al., 2003a). This reduction was proposed to be associated with the formation of larger protein molecules linked by disulfide bridges and/or the interactions of inter/intra proteins *via* other reactive groups during the ageing process. Lipid studies suggested that there was no significant difference in the content of fatty acids (both unsaturated and saturated) in the propanol-water extractable lipid (PWE-L) fraction between fresh and aged rice. In contrast, the content of unsaturated fatty acids in the petroleum ether extractable lipid (PEE-L) fraction of aged rice was lower than that of fresh rice (Zhou et al., 2003b) indicating unsaturated fatty acids in PEE-L fraction are unstable and more likely to be involved in the oxidation than those in PWE-L fraction during a higher temperature storage (Tsuzuki et al., 2014). It has been confirmed that the deterioration of rice grains during storage was caused by lipid peroxidation (Shin et al., 1985), in particular, the existence of lipoxygenase-3 (LOX-3), which is a key enzyme for catalyzing this reaction (Hildebrand, 1989; Suzuki and Matsukura, 1997). These studies might suggest that an efficient direction for improving the storage property of the rice grains is to specifically depress the LOX-3 activity in the endosperm through a genetic engineering or other tools. Griglione et al. (2015) used a fully-automated HS-SPME–GC–MS technique for analyzing the volatile fractions of six high-quality Italian rice cultivars, so as to define volatiles characterizing fingerprints and to identify reliable chemical markers and indices of ageing. They found that, among twenty-five aroma components, some of them showed similar trends over time, including 2-(E)-octenal as a marker of ageing for all the rice cultivars, and heptanal, octanal and 2-ethyl hexanol as cultivar-specific indicators. More importantly, the area ratios 2-acetyl-1-pyrroline/1-octen-3-ol, for rice Venere, and 3-methyl-1-butanol/2-methyl-1-butanol, for rice Apollo could be used as ageing indices. Meanwhile, e-nose system was also applied to study the changes in the volatile profile of rice during storage, and the results indicate that the aromatic compounds seem to be depending on the storage time, regardless of storage temperature (Sung et al., 2014).

Phenolic acids represent a trace component of rice and yet they exhibit some functional properties in rice. The content of bound phenolic acids did not significantly differ during white rice storage, whilst the content of free phenolic acids in the aged rice was lower than that in fresh rice ($P < 0.05$) (Zhou et al., 2014). This may be explained by the chemical reactions between free phenolic acids and unsaturated fatty acids (predominantly in PEE-L fraction) and/or the further cross – linking of phenolic acids with cell wall remnant *via* esterification and etherification, which occurred during the ageing process (Zhou et al., 2014).

4. Effect of ageing process on rice physicochemical property

Rice exhibits very wide ranges of cooking characteristics and rheological properties that are largely determined by the swelling, gelatinization and retrogradation characteristics of its starch (Kong et al., 2015; Zhou et al., 2002b). One of the most sensitive indices of the ageing process in rice is the changes in its pasting properties, as measured by thermoviscometry and particularly amylography (Perdon et al., 1999; Sowbhagya and Bhattacharya, 2001; Toyoshima et al., 1997). Changes in rice pasting and thermal properties following storage have been studied extensively (Likitwattanasade and Hongsprabhas, 2010; Villareal et al., 1976; Zhou et al., 2010), and the results implied that the changes in rice pasting and thermal properties were highly dependent on storage temperature and duration.

Pasting studies indicated that breakdown (BD) and peak viscosity (PV) in RVA viscogram are the most sensitive indices for evaluating rice ageing process (Huang and Lai, 2014; Tananuwong and Malila, 2011). The decrease in breakdown and the gradual disappearance of a clearly defined peak in aged samples were the most notable impacts of ageing (Park et al., 2012; Zhou et al., 2003c). These changes can be attributed to the characteristics of rice grain structure following storage. The study of gelatinization kinetics showed that higher temperature storage resulted in an increase in the breaking point temperature for the aged rice compared to its fresh rice.

The break point (the point at which two straight lines crossed) divides the gelatinization process into two regions: disruption of amorphous region and crystalline region as studied by