ASIAN JOURNAL OF PHARMACEUTICAL AND CLINICAL RESEARCH

INNOVARE ACADEMIC SCIENCES
Knowledge to Innovation

Vol 9, Suppl. 1, 2016

Online - 2455-3891
Print - 0974-2441

Research Article

CHEMICAL CHANGES OF PADDY DURING METAL SILO STORAGE

CHIDANAND DV*, SRINIVASAN K, SHANMUGASUNDARAM S, ALICE RP SUJEETHA J

Indian Institute of Crop Processing Technology, Thanjavur, Tamil Nadu, India. Email: chidanand@iicpt.edu.in

Received: 05 May 2016, Revised and Accepted: 27 May 2016

ABSTRACT

Objective: To study the chemical changes of paddy stored at metal silo for a period of 6-month.

Methods: The peroxide value (PV) and free fatty acids (FFAs) were analyzed by titrimetry method. The total fatty acid profile was analyzed through gas chromatography-mass spectrometry (GC-MS) (Scion 436-GC Bruker model coupled with a triple quadrupole mass spectrophotometer) and National Institute Standard and Technology-MS library.

Results: The PV of paddy at the 1st month of storage is 0.62 mEq/kg and at the 6th month the value increases to 5.11 mEq/kg and initial FFA was recorded as 0.49% and final value of 2.28%. In accordance with these data, the GC-MS study of rice bran oil (RBO) proved that polyunsaturated fatty acid percentage is decreasing over the period of storage time.

Conclusion: With the results and findings, the overall chemical change during the 6-month storage of paddy at metal silo does not affect the RBO quality significantly.

Keywords: Free fatty acids, Peroxide value, Metal silo, Gas chromatography-mass spectrometry.

INTRODUCTION

Grain storage plays an important role in preventing losses which are caused mainly due to weevils, beetles, moths, and rodents [1]. Approximately, over 90% of the government grain is stored in 50-kg bags in state-owned warehouses or in the open air. This has been the practice for decades despite storage losses of more than 10%.

It is estimated that 60-70% of food grain produced in the country is stored at home level in indigenous storage structures. The storage methods range from mud structures to modern bins. The containers are made from a variety of locally available materials differing in design, shape, size, and functions. The materials used include paddy straw, wheat straw, wood, bamboo, reeds, mud, bricks, and cow dung. Grains can be stored indoors, outdoor or at underground level [2].

Thakor *et al*. experimented storing paddy in silo and found that duration of storage had a profound effect on some of the properties and quality of stored paddy grain. Bulk density decreased from 510 to 502 kg/m^3; 1000-grain weight decreased from 19.3 to 18.4 g; germination percentage decreased from 70.6% to 52.3%; insect infestation increased from 4.7% to 18.8%; protein content decreased from 8.78% to 7.89%; ash content of paddy increased from 7.30% to 8.75% in silo storage during storage period of 10-month [3]. Typically, rice during storage undergoes numerous changes in its physical properties and chemical composition, and these changes cause an impact on rice cooking and eating quality [4-6].

Another scenario of storing paddy is aging which increases the volume and water absorption capacity of paddy. During aging of paddy, a number of physiochemical properties of the paddy are subjected to change [6]. Normally, during aging of freshly harvested paddy, there is an increase of rice volume expansion and water absorption observed. The storage conditions are important in the aging process, and they could impact on the number of changes in rice physical properties such as textural properties, pasting, color, flavor, composition, and eating quality [7,8].

Natural contamination of food grains is greatly influenced by environmental factors such as type of storage structure, temperature, pH, and moisture [9]. Types of structure used, length and purpose of storage, grain treatment, and pre-storage practices are all important variables affecting storage losses. The importance of these regional and crop variations immediately determines certain necessary characteristics of crop storage research [10].

Bulk storage systems allow more efficient and easy handling within the processing plant, and better pest control resulting in reduction in quality and quantity losses. In Indian condition, there has been no experimental study on the change of temperature and moisture in paddy stored in metal silo. While many studies on the effect of storage temperature on paddy grain have been reported, as mentioned above, no information is available on physiochemical changes such as free fatty acids (FFAs), peroxide value (PV), and fatty acid profile during storage of paddy in silo at ambient environmental conditions.

METHODS

Source, storage, and sampling of paddy

The paddy (Variety: ADT - 45) of fair average quality (FAQ) was procured from Rice Research Institute, Aduthurai, Tamil Nadu. The procured paddy was analyzed for the FAQ as per the standard procedure given by Food Corporation of India and found satisfactory. Bulk storage of 5-ton quantity of the selected paddy was stored in metal silos (Fig. 1). The paddy samples were collected and analyzed for 6 months of storage.

The brown rice powder was obtained by milling the paddy grain followed by pulverizing and was stored in a cool and dry place.

PV

PV is the measure of the lipid oxidation in foods and it assess the primary oxidative changes in the system. 5 g sample was weighed into a 250 ml stoppered conical flask and 30 ml of acetic acid chloroform mixture was added to it. 0.5 ml saturated potassium iodide solution was added with a Mohr pipette to the solution obtained earlier. It was allowed to stand for 1 minute in dark with occasional shaking and then 30 ml of water was added to it. Following this, titratation was carried out of the liberated iodine with 0.1 N sodium thiosulfate solution, while vigorous shaking until yellow color is almost gone. Furthermore, 0.5 ml

starch solution was added as indicator and the titration was continued with the titrate shaken vigorously to release all iodine from chloroform layer until blue color disappeared. PV expressed as milliequivalent of peroxide oxygen per kg sample (mEq/kg) [11].

PV = (Titre × N × 100/weight of the sample)

Where,

Titre = ml of sodium thiosulfate used and,

N = Normality of sodium thiosulfate solution.

FFA

The acid value is determined by directly titrating the oil in an alcoholic medium against standard potassium hydroxide (KOH) solution. Accurately, weighed appropriate amount of sample is taken in a 250 ml conical flask and 20 ml of freshly neutralized ethanol is added to it, furthermore about 2-3 drops of phenolphthalein indicator is added to the solution. The sample is titrated against 0.1 N KOH solution shaking vigorously during the titration until pale pink color is obtained. The FFA is calculated from acid value and expressed as percent by weight [12].

Acid value = (56.1 × V × N/weight of the sample)

Where,

V = Volume in ml of standard KOH,

N = Normality of the KOH solution.

The acidity is frequently expressed as FFA for which calculation shall be FFA as oliec acid = (28.2 ×V × N/weight of the sample).

Fatty acid profile through gas chromatography-mass spectrometry (GC-MS) instrumentation

Sample preparation

The rice bran oil (RBO) was extracted through soxhlet apparatus with hexane. The oil was methylated with sodium methoxide and extracted with petroleum ether. The ether extract was filtered with sodium sulfate and concentrated through nitrogen flushing. 2 µl of prepared sample was injected into the GC-MS instrument.

Instrumentation

The chemical compositions of brown rice powder were investigated through GC-MS/MS electron ionization (EI) mode. The GC-MS/MS is a scion 436-GC Bruker model coupled with triple quadrupole mass spectrophotometer with fused silica capillary column BR-5 ms (5% diphenyl/95% dimethylpolysiloxane), 30 m × 0.25 mm × 0.25 µm df. Helium gas (99.999%) was used as the carrier gas at a constant flow rate of 1 ml/min and an injection volume of 2 µl was employed (split ratio of 10:1). The column oven temperature program was as follows: 110°C hold for 2 minutes, up to 200°C at the rate of 10°C/min-no hold, up to 280°C at the rate of 5°C/min-9 minutes hold, injector temperature 280°C, total GC running time was 36 minutes. The MS was operated in the positive EI mode with ionization energy of 70 eV. The solvent delay was 0-3.0 minutes. A scan interval of 0.5 seconds and fragments from m/z 50 to 500 Da was programed. The inlet temperature was set at 280°C, source temperature 250°C. The relative percentage amount of each component was calculated by comparing its average peak area to the total areas. Software adopted to handle mass spectra and chromatograms was MS Workstation 8 [13].

Interpretation of components

Detection was performed in total ion capture mode; the peaks were identified and quantified using target ions mass spectra and retention time. Interpretation of chromatogram mass spectrum was done using the database of National Institute Standard and Technology (NIST) having more than 162,000 patterns. The spectrum of the unknown component was compared with the spectrum of the known components stored in the NIST library. The main criteria for selection of suitable ions for an identification of compound should has a high peak area (>0.05%) and should be unique and/or be well resolved from other ions with the same mass to charge ratio (m/z) in the defined time window. Identification of the compounds from the NIST library results was as indicated by the library search program as being more than 80%, more hits and base peak matching. The name, molecular weight, and structure of the components of the test materials were ascertained.

RESULTS AND DISCUSSION

The FFA content during the storage period was calculated at each month intervals. The results are depicted in Fig. 2. From the Fig. 2, it was observed that the FFA percent was increasing with increase in storage periods. This trend is due to lipase activity on the fat present in bran portion of the paddy. It hydrolyses glycerides into acids and thus results in the increasing of fatty acid. The initial FFA was recorded as 0.49% and final value of 2.28% of oleic acid in the 6th month. In general, oils are susceptible to enzymatic hydrolysis; the FFA formed varies with age and storage. FFA determination is a quality marker for establishing the extent of hydrolytic rancidity in oils and fats.

The oxidative stability of paddy grains during storage period was carried out and expressed in terms of PV. Peroxides are the primary oxidation products and its concentration may fluctuate over time since peroxides turn to other oxidation products in time. In general, lower the PV, the better the quality of the storage food grains. From the Fig. 3, it can be observed that there is an increasing trend in PV. The PV content of paddy at the 1st month of storage is 0.62 mEq/kg and at the 6th month the value increases to 5.11 mEq/kg. In mean time, the rise is not exceeding the permissible limit of 10 mEq/kg as prescribed by CODEX

Fig. 1: Metal silo of stored

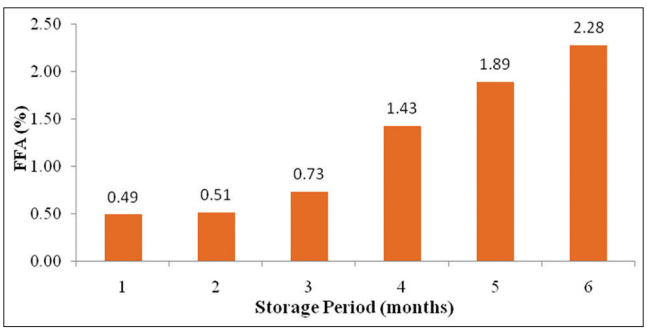

Fig. 2: Variation in free fatty acid value during the storage of paddy in a metal silo for 6 months

alimentarius. It may be due to the contributory effects of antioxidants naturally present in RBO in inhibiting the oxidative rancidity [14].

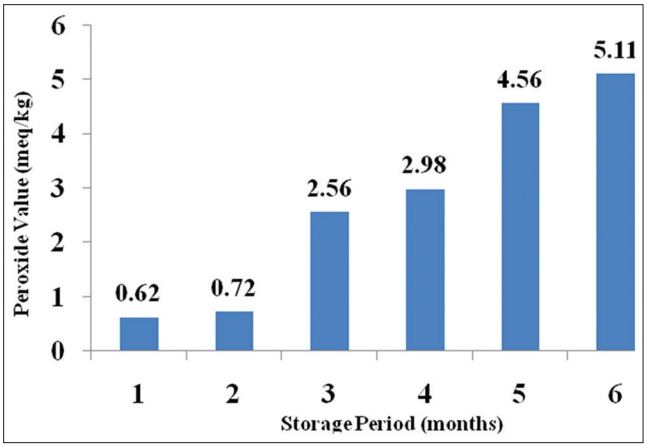

Fig. 3: Variation in peroxide value content of paddy during the 6-month of storage period

Peroxides are useful in assessing the extent to which the rancidity has advanced. Fresh oils usually have PVs below 10 mEq/kg, and a rancid taste often begins to be noticeable when the PV is above 20 mEq/kg (PFA, 2005).

The total ion chromatogram of the paddy samples in all the study period is depicted in Fig. 4. The fatty acids were separated and identified by GC-MS/MS. Oleic, linoleic and palmitic acids were the dominant fatty acids in all the study periods of paddy.

The categories of fatty acids, i.e., saturated fatty acid (SFA), polyunsaturated fatty acid (PUFA), and monounsaturated fatty acid of 6 months of paddy stored in metal silo were illustrated in Figs. 5-7.

The saturated ($C_{12:0}$, $C_{14:0}$, $C_{16:0}$, $C_{18:0}$, $C_{20:0}$, $C_{22:0}$ and $C_{24:0}$) and unsaturated ($C_{16:1}$, $C_{18:1}$, $C_{18:2}$ and $C_{20:1}$) fatty acids detected in the stored paddy grains. The contents of SFA including lauric ($C_{12:0}$), myristic ($C_{14:0}$), palmitic ($C_{16:0}$), stearic ($C_{18:0}$), arachidic ($C_{20:0}$), behenic ($C_{22:0}$), and lignoceric ($C_{24:0}$) acids in the paddy range from 0.11% to 20.45%, respectively. The levels of unsaturated fatty acids, namely, $C_{18:1}$ (oleic acid), $C_{18:2}$ (linoleic acid) and $C_{20:1}$ (gondoic acid) ranged from 0.25% to 42.59%, respectively. It is evident that rice mainly contained linoleic acid

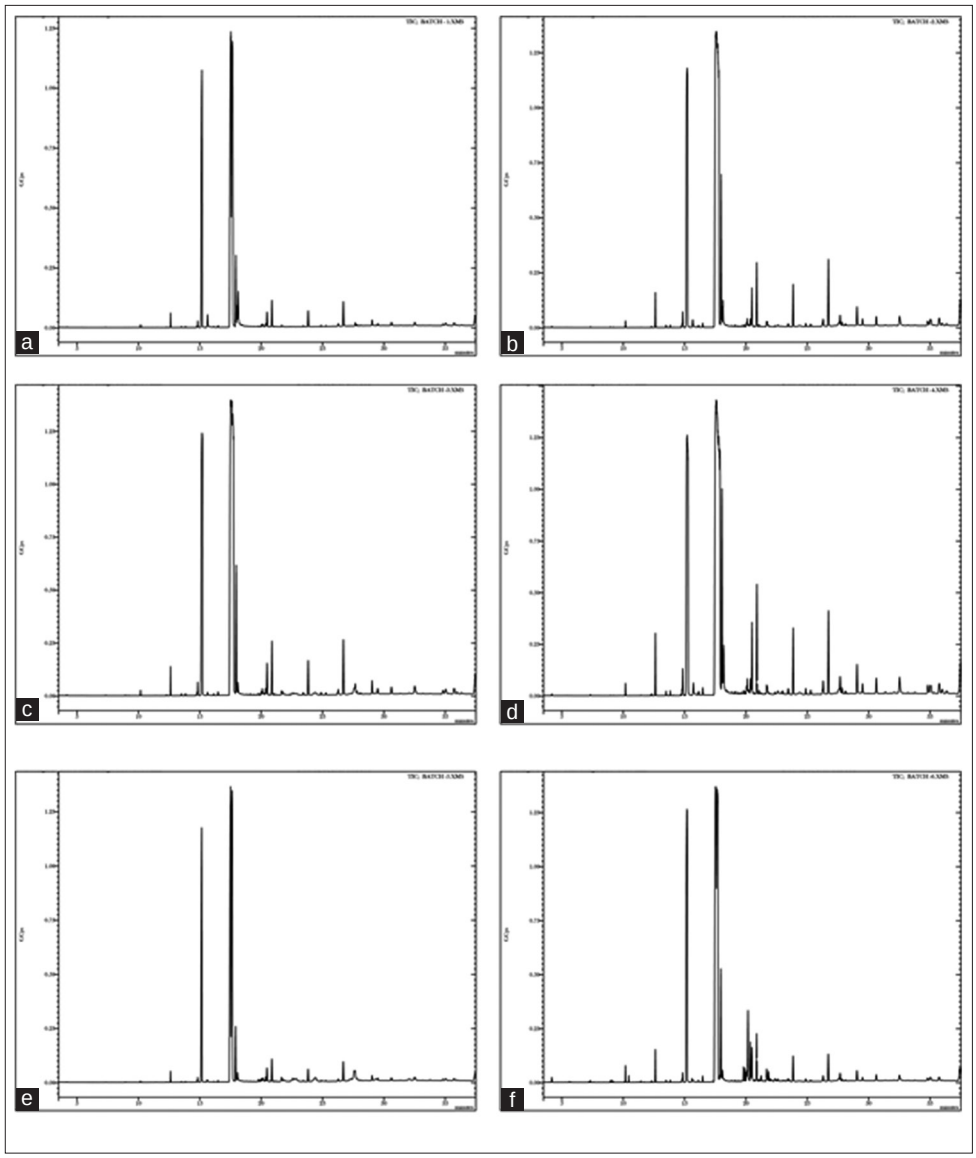

Fig. 4: Gas chromatography mass spectrometry chromatograms of fatty acid profile of rice bran oil during the 6-month storage of paddy. (a-f) The analysis period of months 1-6 respectively

Table 1: Changes in fatty acid composition during 6 months of paddy storage at silo

No.	RT	Name of the compound	GC-MS relative peak area percentage					
			I	II	III	IV	V	VI
1	10.18	Lauric acid methyl ester	0.09	0.16	0.12	0.16	0.17	0.11
2	12.62	Myristic acid methyl ester	0.79	0.84	0.6	0.61	0.74	0.65
3	14.84	Palimtoleic acid methyl ester, (Z)-	0.25	0.54	0.37	0.52	0.31	0.52
4	15.18	Palmitic acid methyl ester	18.8	19.57	20.45	19.49	18.7	19.47
5	15.64	Palmitic acid	0.37	0.38	0.13	0.39	0.41	0.32
6	16.48	Methyl 15-methylpalmitate	0.07	0.15	0.1	0.15	0.11	0.18
7	17.53	Linoleic acid methyl ester	42.25	42.59	41.34	39.26	37.89	34.54
8	17.65	Oleic acid methyl ester, (E)-	27.4	24.06	26.31	26.05	26.95	28.25
9	17.93	Stearic acid, methyl ester	3.04	4.25	4	5.11	4.89	5.44
10	18.13	Gondoic acid	1.54	1.12	0.7	1.88	1.95	2.11
11	20.47	Gondoic acid methyl ester	2.05	1.5	1.04	1.61	1.81	2.09
12	20.87	Arachidic acid methyl ester	1.24	1.48	1.72	1.89	2.28	2.52
13	23.83	Behenic methyl ester	0.79	1.63	1.16	1.11	1.8	2.12
14	26.70	Lignoceric acid methyl ester	1.32	1.73	1.96	1.77	1.99	1.68

I-VI denotes months during storage in metal silo, GC-MS: Gas chromatography mass spectrometry

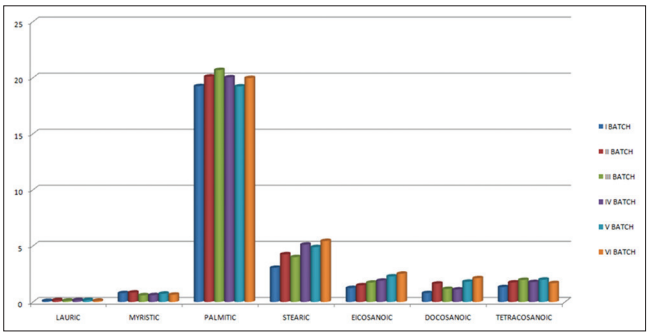

Fig. 5: Categories of saturated fatty acids in the selected paddy

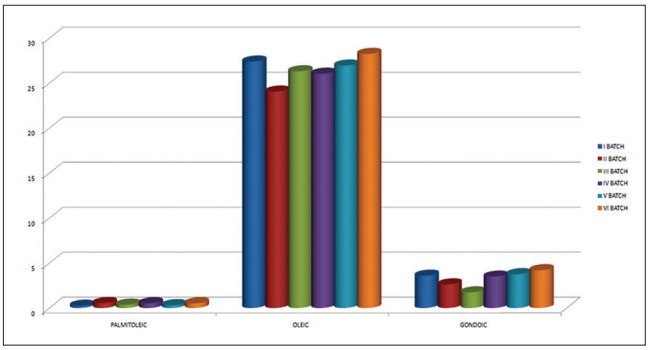

Fig. 6: Categories of mono unsaturated fatty acids in the selected paddy

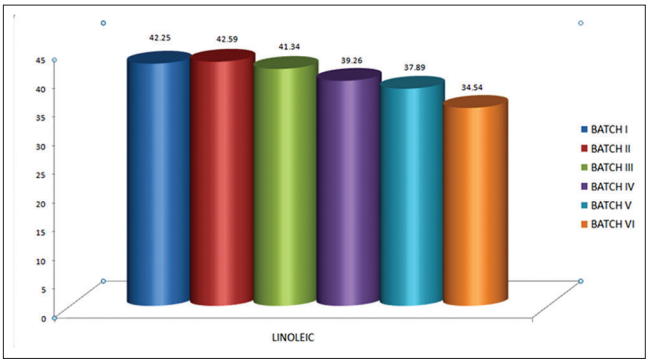

Fig. 7: Categories of poly unsaturated fatty acids in the selected paddy

followed by oleic acid. The concentrations of major fatty acids $C_{18:2}$, $C_{18:1}$, $C_{18:0}$, $C_{16:0}$ of the investigated rice varieties were in close agreement with those reported for the rice bran lipids from Indian based rice [15].

The GC-MS data reveals the fact that the fatty acid composition is not significantly changing with storage period of paddy in metal silo (Table 1). The PUFA content shows a decreasing trend over a time period of storage. This result supports the increasing trend in FFA and PV content of the paddy. Considering the overall fatty acid profile changes, the paddy storage does not affect the RBO quality.

CONCLUSION

With the above research findings and literature evidence, it can be concluded that the paddy storage in metal silo does not affect the rice quality over 6-month of storage period. The physicochemical quality of the paddy in a metal silo for a period of 6-month was almost on par with the initial qualities of paddy and were acceptable. In future, studies need to be conducted at different locations in South India for validate the results for multilocation trials.

REFERENCES

1. Kartikeyan C, Veeraraghavantham D, Karpagam D, Firdouse SA. Traditional storage practices. Indian J Tradit Knowl 2009;8(4):564-8.
2. Singh PK. A decentralized and holistic approach for grain management in India. Curr Sci 2010;99(9):1179-80.
3. Thakor NJ, Patil SC, Sawant AA, Sawant SD. Influence of storage period on physical properties and quality of paddy stored in GIC silo and bag storage under humid Konkan climatic conditions. J Agric Eng 2012;49(1):43-7.
4. Sodhi NS, Singh N, Arora M, Singh J. Changes in physico-chemical, thermal, cooking and textural properties of rice during aging. J Food Process Preserv 2003;27(5):387-400.
5. Patindol J, Wang YJ, Jane JI. Structure functionality changes in starch following rough rice storage. Starch-Stärke 2005;57(5):197-207.
6. Singh N, Kaur L, Sandhu KS, Kaur J, Nishinari K. Relationships between physicochemical, morphological, thermal, rheological properties of rice starches. Food Hydrocoll 2006;20(4):532-42.
7. Teo CH, Karim AA, Cheah PB, Norziah MH, Seow CC. On the roles of protein and starch in the aging of non-waxy rice flour. Food Chem 2000;69(3):229-36.
8. Zhou Z, Robards K, Helliwell S, Blanchard C. Rice aging: Effect of changes in protein on starch behaviour. Starch-Stärke 2003;55(3-4):162-9.
9. Sashidhar RB, Ramakrishna Y, Bhat RV. Moulds and mycotoxins in sorghum stored in traditional containers in India. J Stored Prod Res 1992;28(4):257-60.
10. Greeley M. Appropriate rural technology: Recent Indian experience with farm-level food grain storage research. Food Policy 1978;3(1):39-49.
11. AOAC. Official Methods of Analysis. 18th ed. Gaithersburg, MD, USA: Association of Official Analytical Chemists; 2005.

12. Rajan RG, Krishna AG. Refining of high free fatty acid rice bran oil and its quality characteristics. J Food Lipids 2009;16(4):589-604.
13. Srinivasan K, Sivasubramanain S, Kumaravel S. Phytochemical profiling and GCMS study of *Adhatoda vasica* leaves. Int J Pharm Bio Sci 2014;5(1):714-20.
14. Orthoefer FT, Eastman J. Rice bran oil. In: Champagne ET, editor. Rice: Chemistry and Technology. 2nd ed. Minnesota: American Association of Cereal Chemists Inc; 2004. p. 569.
15. Hemavathy J, Prabhakar JV. Lipid composition of rice (*Oryza sativa* L.) Bran. J Am Oil Chem Soc 1987;64(7):1016-9.