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The Kinetics of Iodine Content Decrease in Fortified Rice During Storage

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Abstract. Iodine Deficiency Disorders (IDD) is a major public health problem in several areas of the world, especially in developing countries. Iodine deficiency can cause goitre, cretinism, decrease of intelligence, mental retardation, brain damage, deaf-mutism, and cause miscarriage in pregnant women and stillbirth as well. The purpose of this research was to determine the stability of the iodine content and determine the kinetics of reaction rate of iodine content decrease in fortified rice during storage. The research was carried out in several steps, i.e. preparation of microcapsules containing iodine, fortification of microencapsulated iodine into rice, determination of iodine content in fortified rice and determination of the kinetics of iodine content decrease in fortified rice during storage. The determination of the kinetics of iodine content decrease in fortified rice was carried out using accelerated self-life test (ASLT) by Arrhenius equation methods. The result showed that the average of kinetics rate of iodine content decrease in fortified rice (k) was $0.0141 \text{ mg kg}^{-1} \text{ hour}^{-1}$ and $1.692 \text{ kcal mol}^{-1} \text{ K}^{-1}$ of activation energy (E_a), which indicated that iodine content (as KIO_3) in fortified rice was fairly stable during storage, although there was still a decrease in iodine content caused by several factors (i.e. temperature, atmosphere, humidity, oxygen and moisture content). The results showed also that the increase in storage temperature can cause the increment of the kinetics value (rate constant) of iodine content decrease. The longest shelf life of fortified rice was 92 days at storage temperature of 25°C .



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6 Introduction

Iodine deficiency disorders (IDD) is still a major public health problem in several areas of the world. Approximately more than 30% of school-aged children suffer from severe deficiency of this micronutrient [1]. Iodine deficiency can cause goitre, cretinism, decrease of intelligence, mental retardation, brain damage, deaf-mutism, and cause miscarriage in pregnant women and stillbirth [2]. The most popular strategy to control iodine deficiency is by incorporating potassium iodate into salt as practiced in some countries. However, because the prevalence of iodine deficiency is still a problem in some countries, other strategies involving large amounts of food consumed need to be considered. Iodization of staple foods such as rice is an interesting approach that has the potential to be applied in many countries. The challenge is maintaining the stability of iodine in the iodized rice, from the storage and distribution to the processing of rice.

Microencapsulation can provide protection against adverse environmental conditions such as high temperature, humidity, light, and reaction with other unwanted materials. Moreover, with microencapsulation the rate of released active ingredients can be controlled (controlled release) so it may extend the availability of iodine [3,4]. Microencapsulation is a process of making microcapsule from active materials in solid form, liquid form, or dispersion, with a thin layer of capsule [5,6,7]. Microencapsulation of iodine is expected to preserve the content of iodine in rice during storage, handling, washing, and cooking.

The kinetics of quality decrease is very important both in the processing and distribution in food. Many researchers have reported the phenomenon of decreases in iodine content in food [8], but most of the studies are still qualitative. The stability of iodine in food is also influenced by the type of food, water content and heating temperature during cooking process, it is decrease levels of iodine during cooking ranged from 36.6% to 86.1% [9,10]. The Iodate content (IO_3^-) in food can be broken down into other iodine species which are iodide (I^-) and iodine (I_2) during process of heating or cooking [11,12].

The effect of temperature on reaction kinetics or stability of iodine in fortified rice can be studied empirically from various aspects such as thermodynamics and statistics. Basically, the logarithmic value of reaction rate constants for iodine content decrease is inversely proportional to the absolute temperature. In other words, the reaction kinetics (k) is affected by the temperature factor [13,14]. This phenomenon is expressed by the Arrhenius equation below:

$$k = k_0 e^{-E_a/RT} \dots\dots\dots (1)$$

$$\ln k = \ln k_0 - \left[\frac{E_a}{R} \right] \frac{1}{T} \dots\dots\dots (2)$$

where :

k_0 = pre-exponential factor,

E_a = activation energy, ie. the extra energy needed by the substrate to achieve a high level probability for the reaction to take place,

R = gas constant (1.986 cal / mol K),

T = temperature (K).

The purpose of this research were to determine the stability of the iodine content and determine the kinetics of reaction rate of iodine content decrease in fortified rice during storage. Besides knowing the factors that influence the stability of the iodine content in fortified rice.

2. Methodology

2.1. Materials

Standard solution CertiPUR of KIO_3 p.a. and KI p.a (Merck, Darmstadt, Germany), maltodextrin, tofu whey powder, aquadest, the sample of fortified rice, amyllum 10%, concentrated H_3PO_4 solution, and $\text{Na}_2\text{S}_2\text{O}_3$ 0,01 N solution.

2.2. Instrumentations

Homogenizer (Micra D9, 40233, Germany), spray dryer (Lab Plant 05, Germany), molen dryer, sprayer, atomizer, vortex mixer, vacuum filter, incubator, membrane filter of 0.45 μm , micro pipette, volumetric flasks, grinder machine, magnetic stirrer, high density polyethylene (HDPE) plastic bag, volumetric pipette, burette and rice whiteness meter.

2.3. Preparation of the microcapsules containing iodine

The microcapsules were prepared by mixing maltodextrin (129.50 g), tofu whey powder (55.5 g), potassium iodate (15 g) and distilled water (800 g) using an ultra-turrax homogenizer at a speed of 11.000 rpm until completely dissolved. The mixture was then kept in a refrigerator overnight to ensure a complete hydration. A quick homogenization was performed for 15 seconds at a speed of 11,000 rpm with a homogenizer prior to spray drying. Spray drying was done at an inlet temperature of 170°C and a feed rate of 15 mL / min.

2.4. Fortification process of microcapsules containing iodine into rice

Fortification was carried out by spraying the suspension of iodine microcapsules using an atomizer during the process of rice polishing. The suspension of iodine microcapsules was prepared by dissolving the microcapsule (70 g) in distilled water (930 mL). Then the microcapsule suspension was atomized by a spraying gun integrated into a rice polishing machine. The incorporation of atomized microcapsule suspension into rice polishing process was controlled so that it gave a flow rate of 0.5 mL /kg/min. The iodized rice (fortified rice) (250 g) was kept in a HDPE plastic bags at different temperatures for a certain period to evaluate the kinetics of iodine decrease during storage.

2.5. Determination of the kinetics of iodine decrease in fortified rice during storage

Fortified rice was packed in HDPE plastic bags and stored for 8 days in an incubator with different temperatures condition at 25°C, 40°C and 65°C. The experiments were done in 3 replications and observations were made at 0, 2, 4, 6 and 8 days of storage. The iodine content was determined by an iodometric method described in the following sub-section. Determination of the kinetic of iodine decrease was done by the accelerated shelf-life test (ASLT) using Arrhenius equation.

2.6. Determination of iodine content in fortified rice

Determination of iodine content in fortified rice was conducted by an iodometric method. Fortified rice samples were powdered using a grinder machine, weighed (25 g) and dispersed in 50 mL of distilled water. The mixture was filtered through membrane filter of 0.45 μm . Concentrated H_3PO_4 (2.5 mL) and KI powder (1 g) were added into the filtrate and mixed until completely dissolved. An indicator solution (amyllum 10%, 1 mL) was added into the mixture and titrated with $\text{Na}_2\text{S}_2\text{O}_3$ (0.01 N) until the blue color in the solution disappeared.

$$\text{Content of KIO}_3 = \frac{\text{volume of titration of Na}_2\text{S}_2\text{O}_3 \times \text{concentration of Na}_2\text{S}_2\text{O}_3 \times 35.67 \times 100\%}{\text{weight of sample (mg)}}$$

3. Results and Discussion

Determination of kinetics of iodine content decrease was carried out in an accelerated shelf-life test (ASLT) experiment at three different temperatures, i.e. 25°C, 40°C, and 65°C for 8 days of storage. The result of research showed that iodine content decreased with the increase in storage time. Calculation results of iodine content decrease in fortified rice at different temperatures and storage time were shown in Table 1. and Figure 1. The kinetics of iodine content decrease are affected by temperature, humidity, oxygen, moisture content, acidity, sunlight, type of packaging, during storage and impurities that are reducing agents or hygroscopic. The method used to determine the kinetics of iodine content decrease in fortified rice was Self-Accelerated Life Test (ASLT).

Table 1. Iodine content decrease in fortified rice at different temperatures and storage time

Storage time (hour)	Temperature (°C)					
	25°C		40°C		65°C	
	Iodine content (mg/kg)	ln C ^a	Iodine content (mg/kg)	ln C ^a	Iodine content (mg/kg)	ln C ^a
0	26.27	3.27	26.27	3.27	26.27	3.27
48	12.85	2.55	14.19	2.65	22.30	3.10
96	10.13	2.31	10.14	2.32	10.84	2.38
144	5.42	1.67	8.12	2.09	6.77	1.91
192	2.71	1.00	0.67	0.00	0.67	0.00

^aln C = decrease of iodine content

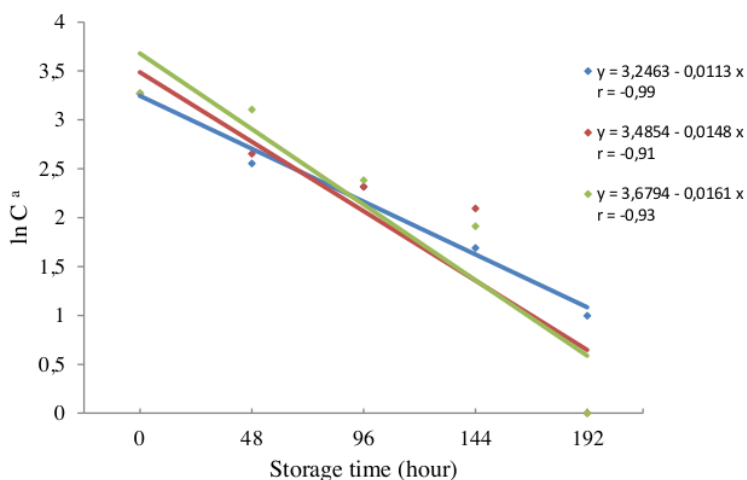


Figure 1. Iodine content decrease in fortified rice (relationship between storage time with ln C) at different temperatures

Kinetics (rate constant) of quality decrease at various temperatures can be calculated based on mathematical calculations using the method according to the Arrhenius theory of reaction kinetics. Basically logarithmic value of the reaction rate constant is proportional to the absolute temperature were shown in Table 2 and Figure 2. In other words, the reaction kinetics (k) is strongly influenced by

the temperature factor. Parameters tested in this research was iodine content decrease in fortified rice. The determination results showed that the kinetics of iodine content decrease in fortified rice was following first order reaction with kinetics of average iodine content decrease (k) was $0.0141 \text{ mg kg}^{-1} \text{ hour}^{-1}$ and the activation energy (E_a) of $1.692 \text{ kcal mol}^{-1} \text{ K}^{-1}$ as shown in Table 3.

Table 2. The relationship between constant of iodine content decrease (k) with temperature ($1/T$)

Temperature	Temperature (T+273)	1/T	k	ln k
25°C	298	0.00336	0.0113	-4.4829
40°C	313	0.00319	0.0148	-4.2131
65°C	338	0.00296	0.0161	-4.1289

$$\text{Activity Energy (Ea)} = 1.986 \text{ kcal/mol k (852)}$$

$$= 1.692 \text{ kkal mol}^{-1} \text{ K}^{-1}$$

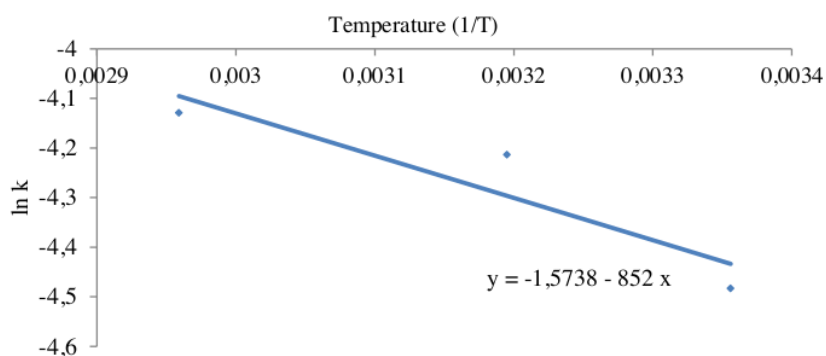


Figure 2. Relationship between $1/T$ with $\ln k$

Table 3. Kinetics of iodine content decrease at different temperatures

Temperature(K)	1/T	Kinetics of iodine content decrease (mg $\text{kg}^{-1} \text{ hour}^{-1}$)
298	0.00336	0.0119
313	0.00319	0.0136
338	0.00296	0.0167
Average		0.0141

The value of k and E_a showed that the iodine was still quite stable in fortified rice during certain storage time, but the presence of water, temperature, reductant and impurities, acids, sun light and type of packaging and inappropriate processing can lead to iodine content decrease (as KIO_3) and will decompose to form species iodide (I^-) and iodine (I_2). Knowledge of the kinetics (rate constant) of the iodine content decrease (k) and activation energy (E_a) can then be used to estimate the amount of iodine levels in the fortified rice using the method according to the Arrhenius reaction kinetics theory. The estimation of the shelf life of fortified rice products can be calculated based on parameter of iodine content decrease [9,10,11,12,13,14,15] as shown in Table 4.

Table 4. Shelf life of iodine in fortified rice at various temperatures

Temperature(K)	Kinetics of iodine content decrease (mg kg ⁻¹ hour ⁻¹)	Shelf life (days)*
298	0.0119	92
313	0.0136	80
338	0.0167	65

*Co/rate constant of iodine content decrease (k)

Since decades ago, rice fortification with various types of additional nutrients has been carried out in developed countries such as America, Japan, the Philippines and Australia. One of the methods used is the enrichment method, this method does not use encapsulation as a protective system for adding vitamins and minerals so that the main drawback of this method is that around 20-100% of additional nutrients can be lost during the rice processing process. The decrease in iodine content in fortified rice during storage is closely related to the properties and characteristics of iodine with the environmental conditions of iodine during storage [16]. Meanwhile, the results showed that fortified rice with the microencapsulation process can maintain the stability of iodine levels ranging from 48.79 - 84.63% stored for 2 days. This depended on storage temperature where each temperature showed a decrease in iodine levels. The higher the temperature and storage time, the greater the decrease in iodine content. Basically, iodine microencapsulation aims to obtain a more stable iodine. The results obtained from iodine microencapsulation produced insoluble microcapsules, thus minimizing the risk of iodine loss due to physical and chemical processes in rice fortification.[17].

Iodine is an essential trace element present in nature. In human nutrition, iodine is an integral part of the thyroid hormones that play an important role in controlling the rate of basic metabolism and reproduction. The rice fortification with microcapsule containing iodine can contribute to decreasing the incidence of simple goiter. The bioavailability of iodide from fortified rice is only 10% of the estimated 0.75 mg iodide in fortified rice consumed per day [18, 19].

4. Conclusion

The rice fortification with microcapsule containing iodine increased the stability of iodine. The results of research showed that the average of kinetics rate of iodine content decrease in fortified rice (k) was 0.0141 mg kg⁻¹hour⁻¹ and 1.692 kcal mol⁻¹K⁻¹ of activation energy (Ea). This suggests that iodine (as KIO₃) in encapsulated ingredients of fortified rice was fairly stable during storage, but there was still a decrease in iodine content caused by several factors (ie. temperature, atmosphere, humidity, oxygen and moisture content). The results showed that the increase in storage temperature causes the increment of the value of kinetics (rate constant) of iodine content decrease. The longest shelf life of fortified rice was 92 days at a storage temperature of 25°C.

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