UNIVERSITI PUTRA MALAYSIA

STORAGE STABILITY AND QUALITY CHARACTERISTICS OF FRIED FISH CRACKERS ADDED WITH RICE BRAN FLOUR AND RESISTANT STARCH

‘ATIQAH ‘AQILAH BINTI IDRIS

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By

'ATIQAH 'AQILAH BINTI IDRIS

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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'ATIQAH 'AQILAH BINTI IDRIS

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Chair : Wan Zunairah binti Wan Ibadullah, PhD
Faculty : Food Science and Technology

Fried fish crackers are very popular traditional snack food in Malaysia and many Southeast Asian countries. However, the main concern is on the deteriorating in fried cracker due to the lipid oxidation, and lipid co-oxidation on the fish protein. The shelf life stability of fried fish cracker is usually less than three months due to lipid oxidation reaction which will result in rancidity, alteration of textural properties and overall degradation of the product quality. Therefore, the aim of the present work was to measure the storage stability and quality characteristics of fried fish crackers added with rice bran flour and resistant starch as influenced by storage temperature.

Fried fish crackers, fish crackers added with 6% (w/w) rice bran flour and fish crackers added with 16.7% (w/w) resistant starch were prepared. The physicochemical properties, lipid stability and protein characteristics were examined at 25, 40 and 60°C for three months. Fried fish crackers were packed into two types of packaging with four different layers of; (i) polyethylene terephthalate-polyethylene-aluminium-linear low density polyethylene (PET-PE-ALU-LLDPE) with 0.5 moisture vapor transmission rate (MVTR) and 0.5 oxygen transmission rate (OTR), and (ii) oriented polypropylene-polyethylene-metallized polyethylene terephthalate-linear low density polyethylene (OPP-PE-MPET-LLDPE) with 0.08 MVTR and 0.08 OTR.

The linear expansion and oil absorption in fried fish cracker was 75.67 ± 5.86% and 27.86 ± 0.79%, respectively. The linear expansion and oil absorption of the fried fish cracker with rice bran and resistant starch was 53.33 ± 2.08%; 18.56 ± 0.39% and 58.00 ± 3.46%; 12.60 ± 1.34% respectively. Physical analysis of fried fish crackers showed decreasing in moisture content (from 4.41 – 5.40% to 2.76 – 3.75%), water

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activity (0.503 to 0.243 a_w), L* and b* value (from 64 to 47 and 29 to 15), and hardness (1.773 to 0.793 kg), while an increase in a* value (0.71 to 5.78) and crispiness (6.94 to 12.45 kg/sec). The fried fish crackers with rice bran showed decreasing in moisture content (ranged from 3.24 – 3.87% to 1.96 – 2.69%), water activity (0.334 to 0.234 a_w), L* value (from 62 to 51), hardness (2.065 to 1.090 kg) and crispiness (12.9 to 8.59 kg/sec), while increased in a* and b* value (from 3.98 to 9.28% and from 16.67 to 23.95% respectively). Physical analyses for fried fish crackers added with resistant starch showed an increase in moisture contents (from 2.75 – 3.47% to 4.08 – 4.54%), water activity (0.297 to 0.436a_w), and a* and b* values (5.27 to 9.14%, and 21.09 to 25.27%, respectively), while a decrease in L* value (from 63 to 58%), hardness (from 2.110 to 1.117 kg) and crispiness (from 12.46 to 8.18 kg/sec) throughout 12 weeks of storage at all temperatures tested.

The lipid yield for fried fish crackers was not stable within the storage time and the concentration of conjugated dienes and thiobarbituric acid reactive substances (TBARS) showed a gradual increase. The lipid yield of the fried fish crackers with rice bran and resistant starch increased within the storage time and the concentration of conjugated dienes and thiobarbituric acid reactive substances gradually decreased. The protein concentration of fried fish crackers and protein oxidation based on carbonyl content gradually increased. The protein concentration and protein oxidation of fried fish crackers with rice bran gradually increased. The protein concentration of fried fish crackers with resistant starch showed a gradual increase while a gradual decrease in protein oxidation. These results showed that fried fish crackers in this storage study had undergone lipid oxidation where there were signs of physical and chemical deterioration observed. In conclusion, it was noted that addition of 6% (w/w) rice bran flour and 16.7% (w/w) of resistant starch in fish crackers that stored at 25°C with suitable packaging materials has given a positive effect on the stability of the fried products.

Keywords: Fried fish crackers, rice bran, unmodified potato starch, physico-chemical analyses, lipid degradation, conjugated dienes, thiobarbituric acid reactive substances, protein concentration, protein oxidation

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KESTABILAN PENYIMPANAN DAN CIRI-CIRI KUALITI KEROPOK IKAN DIGORENG DITAMBAH DENGAN TEPUNG DEDAK BERAS DAN KANJI TAHAN

Oleh

'ATIQAH 'AQILAH BINTI IDRIS

September 2018

Pengerusi : Wan Zunairah binti Wan Ibadullah, PhD
Fakulti : Sains dan Teknologi Makanan

Keropok ikan digoreng adalah makanan ringan tradisional yang sangat popular di Malaysia dan kebanyakkan negara di Asia Tenggara. Walau bagaimanapun, kebimbangan utama adalah kemerosotan keropok ikan digoreng akibat pengoksidaan lipid, dan pengoksidaan lipid pada protein ikan. Kestabilan jangka hayat keropok ikan digoreng biasanya kurang dari tiga bulan akibat tindak balas pengoksidaan lipid yang akan mengakibatkan perubahan bau menjadi tengik, perubahan sifat tekstur dan kemerosotan keseluruhan kualiti produk. Oleh itu, matlamat kajian semasa adalah untuk mengukur kestabilan penyimpanan dan ciri-ciri kualiti keropok ikan digoreng ditambah dengan tepung dedak beras dan kanji tahan yang dipengaruhi oleh suhu.

Keropok ikan digoreng, keropok ikan ditambah dengan 6% (w/w) tepung dedak beras dan keropok ikan ditambah dengan kanji tahan 16.7% (w/w) disediakan. Ciri fizikokimia, kestabilan lipid dan ciri-ciri protein diperiksa pada 25, 40 dan 60 ° C selama tiga bulan. Keropok ikan goreng dibungkus ke dalam dua jenis pembungkusan dengan empat lapisan berbeza; (i) polietilena terephthalate-polietilena-aluminium-linear polietilena ketumpatan rendah (PET-PE-ALU-LLDPE) dengan 0.5 kadar penghantaran wap kelembapan (MVTR) dan 0.5 kadar penghantaran oksigen (OTR), dan (ii) polypropylene- polietilena terephthalate-linear polietilena berketumpatan rendah (OPP-PE-MPET-LLDPE) dengan 0.08 MVTR dan 0.08 OTR.

Pengembangan linear dan penyerapan minyak dalam keropok ikan digoreng masing-masing adalah 75.67 ± 5.86% dan 27.86 ± 0.79%. Pengembangan linear dan penyerapan minyak keropok ikan digoreng dengan dedak beras dan kanji tahan masing-

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masing adalah 53.33 ± 2.08%; 18.56 ± 0.39% dan 58.00 ± 3.46%; 12.60 ± 1.34%. Analisa fizikal keropok ikan digoreng menunjukkan penurunan dalam kandungan lembapan (dari 4.41 - 5.40% hingga 2.76 - 3.75%), aktiviti air (0.503 hingga 0.243 a_w), L* dan nilai b* (dari 64 kepada 47 dan 29 hingga 15) dan kekerasan (1.773 hingga 0.793 kg), manakala peningkatan dalam a* nilai (0.71 hingga 5.78) dan kerangupan (6.94 hingga 12.45 kg/saat). Keropok ikan digoreng dengan dedak beras menunjukkan penurunan kandungan lembapan (purata antara 3.24 - 3.87% hingga 1.96 - 2.69%), aktiviti air (0.334 hingga 0.234 a_w), nilai L* (dari 62 hingga 51), kekerasan (2.065 hingga 1.090 kg) dan kerangupan (12.9 hingga 8.59 kg / sec), manakala peningkatan dalam a* dan nilai b* (dari 3.98 hingga 9.28% dan dari 16.67 hingga 23.95%). Analisis fizikal untuk keropok ikan digoreng ditambah dengan kanji tahan menunjukkan peningkatan kandungan lembapan (dari 2.75 - 3.47% hingga 4.08 - 4.54%), aktiviti air (0.297 hingga 0.436a_w), dan nilai a* dan b* (5.27 hingga 9.14%, dan 21.09 hingga 25.27%), manakala penurunan nilai L* (dari 63 kepada 58%), kekerasan (dari 2.110 hingga 1.117 kg) dan kerangupan (dari 12.46 hingga 8.18 kg/saat) sepanjang 12 minggu penyimpanan semua suhu yang diuji.

Hasil lipid untuk keropok ikan digoreng tidak stabil dalam masa penyimpanan dan kepekatan konjugated dienes dan bahan reaktif asid thiobarbituric (TBARS) menunjukkan peningkatan beransur-ansur. Hasil lipid dari keropok ikan digoreng ditambah dengan dedak beras dan kanji tahan meningkat dalam masa penyimpanan dan kepekatan konjugated dienes dan bahan reaktif asid thiobarbituric secara beransur-ansur menurun. Kepekatan protin keropok ikan digoreng dan pengoksidaan protin berdasarkan kandungan karbonil meningkat secara beransur-ansur. Kepekatan protin dan pengoksidaan protein keropok ikan digoreng ditambah dengan dedak beras meningkat secara beransur-ansur. Kepekatan protein keropok ikan digoreng ditambah dengan kanji tahan menunjukkan peningkatan beransur-ansur sementara penurunan secara beransur-ansur dalam pengoksidaan protein. Keputusan ini menunjukkan bahawa keropok ikan digoreng dalam kajian penyimpanan ini telah menjalani pengoksidaan lipid di mana terdapat tanda-tanda kemerosotan fizikal dan kimia. Kesimpulannya, penambahan 6% (w/w) tepung dedak beras dan 16.7% (w/w) kanji tahan dalam keropok ikan yang disimpan pada suhu 25°C dengan bahan pembungkusan yang sesuai memberi kesan positif ke atas kestabilan produk bergoreng.

Kata kunci: Keropok ikan yang digoreng; dedak padi; kanji kentang yang tidak diubahsuai; analisis fiziko-kimia; degradasi lipid; conjugated dienes; bahan reaktif asid thiobarbituric; kepekatan protein; pengoksidaan protein.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

Wan Zunairah binti Wan Ibadullah, PhD
Senior Lecturer
Faculty of Food Science and Technology
Universiti Putra Malaysia
(Chairman)

Nazamid b. Saari, PhD
Professor
Faculty of Food Science and Technology
Universiti Putra Malaysia
(Member)

Nor Afizah binti Mustapha, PhD
Senior Lecturer
Faculty of Food Science and Technology
Universiti Putra Malaysia
(Member)

_____
ROBIAH BINTI YUNUS, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

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Name and Matric No.: ‘Atiqah ‘Aqilah binti Idris (GS41808)

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Signature: _____
Name of Chairman of Supervisory Committee: Dr. Wan Zunairah binti Wan Ibadullah

Signature: _____
Name of Member of Supervisory Committee: Prof. Nazamid bin Saari

Signature: _____
Name of Member of Supervisory Committee: Dr. Nor Afizah binti Mustapha

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LIST OF ABBREVIATIONS

%	Percentage
≈	Approximately
°C	Degree celsius
<	Less than
α	alpha
aw	Water activity
BHA	Butylated hydroxyanisole
BHT	Butylated hydroxytoluene
BOPP	Biaxially oriented polypropylene
BON	Biaxially oriented nylon
BSA	Bovine serum albumine
CD	Conjugated dienes
cm	Centimeter
CO_2	Carbon dioxide
Cu^+	Copper
$CHCl_3$	chloroform
DNPH	Dinitrophenylhydrazine
EDTA	Ethylenediaminetetraacetic acid
FAMA	Federal Agricultural Marketing Authority
g	Gram
g/kg	Gram per kilogram
h	Hour
HDPE	High density polyethylene
kg	Kilogram
kg/sec	Kilogram per seconds
L*	Alkyl radical
LO*	Alkoxyl radical
LOO*	Peroxide radical
LOOH	Hydroperoxide
LDPE	Low density polyethylene

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LLDPE	Linear low density polyethylene
MDA	Malondialdehyde
MDPE	Medium density polyethylene
m	Meter
min	Minute
mg/mL	Milligram per milliliter
mL	Milliliter
mL/g	Milliliter per gram
mm	Millimeter
mm/sec	Millimetre per second
MSG	Monosodium glutamate
MVTR	Moisture vapor transmission rate
µL	Microliter
µm	Micrometer
µM	Micromolar
µM/µL	Micrometer per microliter
N_2	Nitrogen
nm	Nanometer
nmol/mg	Nanomol per milligram
O_2	Oxygen
OTR	Oxygen transmission rate
OPP	Oriented polypropylene
OPP-PE-MPET-LLDPE	oriented polypropylene-polyethylene-metallized polyethylene terephthalate-linear low density polyethylene
PBS	Phosphate buffered saline
PE	Polyethylene
PET	Polyester
PP	Polypropylene
PET-PE-ALU-LLDPE	polyethylene terephthalate-polyethylene-aluminium-linear low density polyethylene
PVDC/PVC	Polyvinylidene chloride
rpm	Revolutions per minute
RS	Resistant starch
sec	Second

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SDS	Sodium dodecyl sulfate
SiOx	Silicon oxide
TBARS	2-Thiobarbituric Acid Reactive Substances assay
TBHQ	Tertiary butylhydroquinone
TCA	Trichloroacetic acid
USD	United States Dollar
UV	Ultraviolet
w/w	Weight per weight

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CHAPTER 1

INTRODUCTION

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1.1 General Overview

Shelf-life is defined as the duration of the food product when keeping under the advocated situations will maintain its safety, retain its sensory quality, chemical, physical and microbiological characteristics, and comply with the label declaration of nutritional data (Kilcast and Subramaniam, 2000). Fried fish crackers have long shelf-life due to the low moisture content (3-4%) and if properly packaged in moisture, oxygen, and light barrier packaging materials. During frying, the frying oil and oxidation products will be absorbed by fried foods. Then, during transport and storage, the lipid oxidation is catalyzed by hydroperoxides and other oxidation products in the oil thus cause fried foods highly prone to oxidation. The shelf-life of fried foods reduced and the volatile compounds cause off-flavors and odors mainly formed during auto-oxidation in storage (Hwang and Winkler-Moser, 2016).

Lipid oxidation in foods can be characterized as oxidative stability, oxidative deterioration, or oxidative rancidity of oils/fats during processing or storage (Skibsted, 2010). The quality of foods such as color, odor, taste, and palatability may be decreased by lipid oxidation. The levels of nutrients such as essential fatty acids, essential amino acids, and vitamins may also decrease, and may also cause the production of toxic compounds (Hu, 2016). There are internal (intrinsic) factors that influence oxidative stability of oils/fat-containing foods such as the moisture content, type of food matrices, protein, water activity, as well as the quality of ingredients containing the oils/fats. Lipid oxidation effect from the external (extrinsic) factors is including temperature, air (oxygen), light, enzymes, transition metals, processing and storage conditions, antioxidants, the ratio of surface area to oils/fats volume, packaging, and environmental and systematic pHs (Hu, 2016).

The situation is made more complicated by the presence of co-oxidations in complex foods, in which other system components; especially proteins react with lipid oxidation radicals and secondary products (Schaich, 2016). Starches may also react with lipid oxidation products (Schaich, 2014; Hwang and Winkler-Moser, 2016). Oxidation can be transfer to other molecules in the food system by co-oxidations. Simultaneously, it will consume lipid oxidation intermediates and products. Lipid oxidation seems to be low or inhibited under these conditions. In reality, it is swiftly and actively transmitting oxidation to other molecules. Consequently, to determine the full extent of oxidative

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degradation and to refrain from underestimating lipid oxidation, measuring the co-oxidation suitable for the food system must be included (Schaich, 2016).

Rice bran has various applications in food industries among which are to increase the nutritional quality of processed foods. Rice bran has some health advantages which are cholesterol-lowering properties, cardiovascular-health benefits and anti-tumor activities (Tuncel et al., 2014). Potato starch has been used widely in a variety of food systems and is special amongst other commercial starches (e.g. cereal types) (Yusuph et al., 2003). Potato starch is classified as RS_2 (Englyst et al., 1992). RS_2 is the excess of starch that digested very slowly and incompletely in the small intestine. They allow the formation of low-bulk high-fiber products with improved texture, appearance, and mouth feel (such as better organoleptic qualities) compared with traditional high-fiber product (Sajilata et al., 2006).

1.2 Problem Statement

Lipid oxidation limits the shelf-life of crackers consequently destroying the palatability of foods and may alter the physical properties and potentially forms toxic compounds. Adding functional ingredients such as rice bran flour and resistant starch may reduce the lipid oxidation while maintaining the quality of the product.

1.3 Objectives of Study

The main objective of this study is to investigate the effect of storage stability and quality characteristic of fried fish crackers incorporated with rice bran flour and resistant starch as influenced by storage temperatures.

The specific objectives of this study were:

1) To study the quality changes of fried fish crackers as influenced by storage temperature.
2) To investigate the effect of rice bran flour addition on oxidative stability of fried fish crackers as influenced by storage temperatures.
3) To evaluate the effect of resistant starch addition on oxidative stability of fried fish crackers as influenced by storage temperatures.

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