

**INFLUENCE OF STORAGE CONDITIONS ON
MOISTURE SORPTION ISOTHERM,
LIPID OXIDATION AND OFF-ODOR EVALUATION
OF DRY FOOD MODELS**

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ผลของสภาวะในการเก็บรักษาต่อพฤติกรรมการดูดคายความชื้น
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EVALUATION OF DRY FOOD MODELS**

Suranaree University of Technology has approved this thesis submitted in partial fulfillment of the requirements for a Master's Degree.

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การศึกษาพฤติกรรมการดูดและคายความชื้นของอาหารแห้งทางการค้า แบ่งตามแหล่งของโปรตีนที่แตกต่างกันออกเป็น 2 ชนิด (เอและบี) ในแต่ละชนิดแบ่งออกเป็น ประเภทที่มีโปรตีนและไขมันเป็นองค์ประกอบในปริมาณปกติและปริมาณสูง อาหารแห้งทุกชนิดที่ศึกษามีขนาดและรูปร่างที่แตกต่างกัน พฤติกรรมการดูดและคายความชื้นของอาหารแห้งทางการค้ามีความสัมพันธ์ระหว่างปริมาณความชื้นที่สภาวะสมดุลและปริมาณน้ำอิสระจัดอยู่ในรูปแบบที่ 2 ตามทฤษฎีการดูดซับไอน้ำของสารดูดซับ ปริมาณความชื้นที่สภาวะสมดุลของอาหารชนิดแห้งมีปริมาณเพิ่มขึ้นเมื่อปริมาณน้ำอิสระเพิ่มขึ้น แต่เมื่ออุณหภูมิเพิ่มขึ้นปริมาณความชื้นที่สภาวะสมดุลของอาหารแห้งและความแตกต่างของปริมาณความชื้นที่สภาวะสมดุลระหว่างกระบวนการดูดความชื้นและกระบวนการคายความชื้นจะมีปริมาณลดลง พฤติกรรมการดูดและคายความชื้นของอาหารแห้งทุกชนิดที่ศึกษาทำนายโดยใช้แบบสมการกุกเกิลแฮม แอนเดอร์สัน ดิบอร์ (Guggenheim-Anderson-DeBoer, GAB) ค่าความชื้นระดับขั้นแรกของอาหารคำนวณโดยใช้แบบสมการบลูเนอร์ เอลเมท์ เทลเลอร์ (Brunauer-Emmett-Teller, BET) ค่าพลังงานทางอุณหพลศาสตร์ที่เกี่ยวข้องกับกระบวนการดูดและคายความชื้นของอาหารแห้งทางการค้าที่นำมาศึกษา คือ ไอโซสเทอริกฮีต (Isosteric heat) และเอนโทรปี (Entropy) มีแนวโน้มลดลงเมื่อปริมาณความชื้นในอาหารสูงขึ้น

การเกิดออกซิเดชันของไขมันในอาหารแห้ง ได้ศึกษาเปรียบเทียบปริมาณของสารต้านการเกิดออกซิเดชัน (บิวทิเรตไฮดรอกซีแอนิโซลและบิวทิเรตไฮดรอกซีโทลูอิน) ที่อุณหภูมิ 35, 45 และ 55 องศาเซลเซียส พบว่าสูตรอาหารแห้งที่มีการเติมสารต้านการเกิดออกซิเดชันตามปริมาณทางการค้า มีปริมาณอนุพันธ์ของสารที่ทำปฏิกิริยากับกรดไทโอบาบิฟูริกและปริมาณเฮกซาเนลอยู่ในระดับที่ต่ำกว่าสูตรอาหารแห้งที่มีปริมาณสารต้านการเกิดออกซิเดชันอยู่ในระดับที่ต่ำมาก ปริมาณผลิตภัณฑ์ที่เกิดจากออกซิเดชันของไขมันจะมีปริมาณสูงขึ้นเมื่ออุณหภูมิเพิ่มขึ้น ส่วนการเกิดออกซิเดชันของไขมันในอาหารแห้งทางการค้าทั้งสี่ชนิด พบว่าปริมาณของอนุพันธ์ของสารที่ทำปฏิกิริยากับกรดไทโอบาบิฟูริกและปริมาณของเฮกซาเนลมีค่าเพิ่มขึ้นตามการเพิ่มขึ้นของอุณหภูมิและระยะเวลาในการเก็บ ระดับการเปลี่ยนแปลงของตัวชี้วัดทั้งสองแสดงให้เห็นถึงความ

แตกต่างของการเกิดออกซิเดชันของไขมันระหว่างอาหารแห้งทางการค้าที่มีแหล่งของโปรตีนต่างกัน การเกิดออกซิเดชันของไขมันในอาหารแห้งทางการค้า เมื่อเก็บที่อุณหภูมิ 32 องศาเซลเซียสเป็นเวลานาน 18 เดือน พบว่ามีปริมาณของอนุพันธ์ของสารที่ทำปฏิกิริยากับกรดไทโอโอบาบิฟูริกอยู่ในระดับต่ำและตรวจไม่พบปริมาณของเฮกซาแนลตลอดระยะเวลาการเก็บรักษา การตรวจสอบกลิ่นผิดปกติในอาหารแห้งที่มีปริมาณของสารด้านการเกิดออกซิเดชันตามปริมาณปกติและเติมในปริมาณที่ต่ำมาก พบว่ามีกลิ่นผิดปกติมีระดับสูงขึ้นตามอุณหภูมิที่เพิ่มขึ้นและกลิ่นผิดปกติของอาหารแห้งที่มีการเติมสารด้านการเกิดออกซิเดชันอยู่ในระดับที่ต่ำมากจะมีกลิ่นคล้ายกับกลิ่นของเฮกซาแนล ส่วนอาหารแห้งทางการค้าทั้งสี่ชนิดมีระดับของกลิ่นผิดปกติไม่แตกต่างกัน ระดับความเข้มข้นของอนุพันธ์ของสารที่ทำปฏิกิริยากับกรดไทโอโอบาบิฟูริกและเฮกซาแนลที่ผู้บริโภครู้สึกได้ยอมรับ คือ 4.8 ไมโครกรัมต่อกรัม และ 1.67 นาโนกรัมต่อกรัม ตามลำดับ

สาขาวิชาเทคโนโลยีอาหาร

ปีการศึกษา 2550

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ลายมือชื่ออาจารย์ที่ปรึกษาร่วม_____

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PIYAPORN NEAMSUNGNOEN : INFLUENCE OF STORAGE CONDITIONS
ON MOISTURE SORPTION ISOTHERM, LIPID OXIDATION AND OFF-
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ASST. PROF. WEERASAK LERTSIRIYOTHIN, Ph.D., 119 PP.

DRY FOOD/SORPTION ISOTHERM/HYSTERESIS/ENTHALPY-ENTROPY/
LIPID OXIDATION/OFF-ODOR

Moisture adsorption and desorption isotherms of commercial dry food models were determined. Commercial dry food models were divided by different sources of protein into two types (model A and B) and each model was sub-grouped into normal and high protein/fat content. Besides, all of dry food models were different in their shapes and sizes. The relationship between equilibrium moisture content (EMC) and water activity of all the testing dry food models was found to fall into the category of type II sorption isotherm. At a constant storage temperature, the EMC of all dry food models was increased with an increasing water activity. The EMC was a decreasing function of storage temperature. The EMC differences between adsorption and desorption for every testing dry food models were gradually decreased when the storage temperature rose. Guggenheim – Anderson - DeBoer (GAB) model was identified as the best mathematical expression for the moisture sorption characteristic of the testing products. The monolayer moisture contents of all the testing dry food models were determined using the Brunauer-Emmett-Teller (BET) model. Thermodynamic properties of the moisture sorption process, isosteric heat of sorption and entropy of sorption, were non-linear decreasing functions with equilibrium moisture content for both moisture adsorption and desorption.

Lipid oxidation of all the testing dry food models was examined to compare the effect of antioxidant loading and to evaluate the effect of storage temperature (35, 45 and 55°C). It was then found that the commercial used formula (CUF) demonstrated much lower levels of thiobabaturic acid reactive substances (TBARS) and hexanal contents than those of the minimum or inevitable adding level of BHA/BHT formula (IAF) and the lipid oxidation products were clearly increased with a rise in storage temperature. TBARS and hexanal contents of all the four testing commercial dry food models also increased with the increasing temperature and storage time. The lipid oxidation products were changed at a different level between the dry food models A and B due to the differences in their protein sources. For a long term storage condition (32°C for 18 months), all of the testing commercial dry food models demonstrated very low levels of TBARS and there was no detection of hexanal throughout the storage period. Off-odor intensity of CUF and IAF samples was increased with the increasing storage time and temperature and the off-odor of the IAF sample was also noticed as hexanal - like odor. Moreover, the off-odor intensity among the four testing commercial dry food models under the same storage condition statistically showed no significant differences. The corresponding levels of TBARS and hexanal to the panelists' off-odor rejection limit were set at 4.8 µg/g and 1.67 ng/g, respectively.

School of Food Technology

Academic Year 2007

Student's Signature_____

Advisor's Signature_____

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Co-advisor's Signature_____

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LIST OF ABBREVIATIONS

a	=	Constant (isotherm model)
a_w	=	Water activity
b	=	Constant (isotherm model)
C	=	Constant (isotherm model)
CUF	=	Commercial use formula (full load of BHA and BHT)
df	=	Degree of freedom
E_a	=	Activation energy (kJ/mol)
ΔG	=	Gibbs free energy (kJ/mol)
ΔH	=	Enthalpy of sorption (kJ/g K)
ΔS	=	Entropy of sorption (J/g K)
%EMC	=	Equilibrium moisture content (%)
IAF	=	Inevitable adding formula (a minute load of BHA and BHT)
K	=	Constant (isotherm model)
λ	=	Latent heat of vaporization (2417.87 J/ mol K)
M	=	Moisture content
m_0	=	Monolayer moisture content
MDA	=	Malondialdehyde
M_e	=	Moisture content (experiment)
M_p	=	Moisture content (predicted value)
MRE	=	Mean relative error
\bar{m}	=	Average moisture content

LIST OF ABBREVIATIONS (Continued)

N	=	Number of experimental data
q^{net}	=	Net isosteric heat of sorption (kJ / mol K)
R	=	Universal gas constant (0.462 J/ g K)
R^2	=	Regression coefficient
RSS	=	Residual sum of square
SEE	=	Standard error of estimate
T	=	Temperature (K)
TBARS	=	Thiobarbituric acid reactive substance
TEP	=	1,1,3,3,-tetraethoxypropane
W_e	=	Sample weight at equilibrium (g)
W_d	=	Sample weight at equilibrium after drying (g)

CHAPTER I

INTRODUCTION

1.1 Introduction

Dry food industries are continuously growing for a long time with very high competition to produce high quality products. Consumer attempts to prepare a high nutritious dry food and it is often required a cooking time. Therefore new dry foods are produced to give a convenience for consumers and more nutritional value. Foods are divided into 4 types; there are dry foods, semi-moist or soft foods, snack foods and canned or frozen foods. Besides that, they were classified by a level of moisture content as a dry food and wet food.

Nowadays, dry foods are the most desirable ones due to high in nutritional and convenience for consumption. Commonly raw materials used in dry food products are corn starch, wheat starch, chicken and beef. Besides that dry foods contain other ingredients and food additives to improve their taste and quality preservation. Although, dry foods normally have a longer shelf life in term of microbial stability than the wet ones, other deterioration also occurred. Thus knowledge in production, product stability, distribution and storage conditions are needed for evaluation of shelf life stability. The changes of moisture content are important to quality and stability of dry food due to its physical and chemical changes. Storage conditions in term of heat and humidity have a direct effect on moisture adsorption and desorption behaviors. Therefore, understanding the relationship between the changes of dry food product

under various storage conditions is useful for prediction the quality and selecting the suitable preservative and packaging materials Furthermore, the important chemical reaction including lipid oxidation is affected by moisture changing and resulting in flavor, color and textural alteration. The extrusion cooking may cause of hydrolytic and oxidative rancidity which both of reactions affect consumer perception (Lin, Hsieh, and Huff, 1998). Moreover, the physical changes during extrusion process including expanded porous of extruded products are susceptible to oxidation during storage or transportation.

Dry foods are classified as ready-to-eat (RTE) products which produced through extrusion process. Low moisture foods and high content of unsaturated fatty acid are susceptible for oxidations that evaluate the product off-flavor during storage. Thus water content and storage condition of dry food products are stressed for minimizing oxidation in order to long shelf life and high product quality. The acceptances of dry foods are critical due to many quality attributes are attack to consumer acceptance including texture, taste, off-flavor and color (Mazumder, Roopa, and Bhattacharya, 2007). Low moisture foods and expansion of dry food products respect to hard or crispness of the product and these characteristics are affected by the level of moisture content or water activity of storage condition.

Thus the moisture content of dry product and storage condition are important factors for quality control. Moisture content has an affecting on sensory acceptance of dry food such as taste, texture and overall appearance. The movements of ingredient or food compositions are affected by moisture level that increase or decrease chemical reaction. Even though low moisture foods are fewer hazards from microbial growth but the problem of oxidation may takes place. The optimum water activity must be

concern due to extending of product quality along with stability throughout storage time. According to various storage conditions have direct effect on product quality, therefore study on moisture changes at a variety of storage conditions are necessary for quality assessment. Besides that moisture changing behavior is used as an implement for selecting and designing the appropriated packaging materials.

Dry food products are high starch and protein containing along with expansion process and create many available of sorption sites. As a result these products are high moisture sorption properties in order to textural changes and initiate lipid reaction. The alteration of dry food both of textural and flavor are effect on product acceptance. Thus knowledge in moisture sorption behaviors of dry products is crucial for product development and evaluated for longer shelf-life (Alhamdan and Hassan, 1999). Moisture sorption isotherm is importance for drying process design, selecting suitable packaging material and shelf-life prediction at the different storage conditions. Moisture sorption isotherm usually study for dehydrated foods including cookies, cereals and starch based snack foods due to most deterioration rate are depend on moisture sorption behavior (Maskan and Gogus, 1999; Kaleemullah and Kailappan, 2004). Furthermore, the problems of off-odor might be the result of lipid or protein degradation including lipid oxidation of fat-containing foods and respect to loss of nutrients (Wikes et al., 2000). As the problem of dry food products, moisture content is the main factor of deterioration. Thus study the relationship between water content in food equilibrium with water activity or relative humidity of air at constant temperature and pressure are valuable for predicting deterioration rate of dry food products (Kaymak-Ertekin and Gedik, 2004).

Most of dry foods are produced by extrusion cooking which high expansion and porosity that respect to more available of sorption sites and leading to product deterioration. For example, high water activity condition, these products tend to absorbed moisture from surrounding as a result increasing moisture content and decreasing in product quality due to changing of texture, color and product flavor (Dorakova and Menkob, 2004). Thus the water activity of environment and food products are most important factor for dry food products because it used as a tool for estimating the chemical reaction, and the problem of microbial growth (Labuza, Lannane, and Chen, 1985). Therefore shelf life stability of foods depends on moisture migration or water diffusion rate which effect on quality of food especially complex food was stored at various storage conditions (Risbo, 2003).

Moisture sorption isotherm behaviors are depending on their composition and processing. The mathematical models were evaluated for describing moisture sorption isotherm which gave more advantages such as convenience for design drying process, shelf life prediction and packaging material selection. However, no mathematical model can describe accuracy isotherm behaviors for all food types due to complexity of food products (Cassini, Marczak, and Norena, 2005). The Guggenheim-Anderson deBoer (GAB equation) widely used for sorption isotherm prediction and this model base on sorption layer until reach equilibrium and describes cover the wide range of water activity (Kaymak-Ertekin and Sultanoglu, 2001; Lahsasni, Kouhila and Mahrouz, 2004; Mederios, 2005) Moreover, the deterioration rate not depend on only water content but their involved with another reaction such as oxidation of their compositions. The lipid reaction are affecting by fat-containing and storage conditions so the degree of oxidation should be studied along with moisture changing. Because

of substrate migration was affected by amount of water content which stimulates lipid reaction. Lipid oxidation used as an indicator for quality and shelf life determinations because it effect on off-flavor, tastes and decreasing in consumer acceptance (Lin, Hsieh and Hoff, 1998).

This research was to study the moisture sorption isotherm of dry food models and to evaluate a potential off-odor caused by lipid oxidation in the dry food models. The best mathematical models were selected for describing the sorption isotherm behaviors. The lipid oxidation of these products was determined via chemical analysis. Moreover, the sensory evaluation was studied using only off-odor perception to judge the consumer acceptance of these particular dry food models.

1.2 Research hypothesis

1.2.1 Moisture sorption isotherm of dry food models represent sigmoid shape and water content depends on storage conditions.

1.2.2 Off-odor of dry food models were created from oxidation of their composition especially amount of fat containing and storage conditions.

1.3 Research objectives

1.3.1 To study the moisture adsorption and desorption isotherms and determine the effect of temperature on isotherms of dry food models.

1.3.2 To study the effect of temperature on lipid oxidation occurred in dry food models and conduct human's off-odor perception of dry food models.

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CHAPTER II

LITERATURE REVIEWS

2.1 Moisture adsorption and desorption

2.1.1 Water activity

Water is the major component in food and biological materials, providing predominant role in physical and chemical properties. The amounts of moisture content of food products are set based on food types. Water is an important factor to food properties because it can bind with other food components through various chemical bonding such as ionic, covalent and hydrogen bonding that effect on the solubility and transition state of food (Lewicki, 1997). Moreover, water is also significant to quality changes during production, storage, transportation and distribution to consumers, since water play an important role on the mass transfer, chemical reactivity and activity of microorganisms. The interactions between water and solutes create many bond strengths including water-ions and ionic group, water-natural group (hydrogen bonding) and water-non polar substance (Fennema, 1985). The water molecule contains hydrogen and oxygen atoms as seen in Fig 2.1 which initiate covalent or hydrogen binding with food components such as hydroxyl group of polysaccharide, carbonyl and amino groups of protein, and polar groups of other components (Rockland and Beuchat, 1987).

Many chemical bonding between water and food components are found in food system, bond strength depends on water content and type of food components. For

example, water molecules are tightly bound at low moisture content and promoting the chemical bonding with protein or carbohydrate. In case of low moisture food, it is difficult to remove all water content due to tightly bound, resulting in a relatively high temperature requirement needed for bond breaking in order to remove such as amount of moisture.

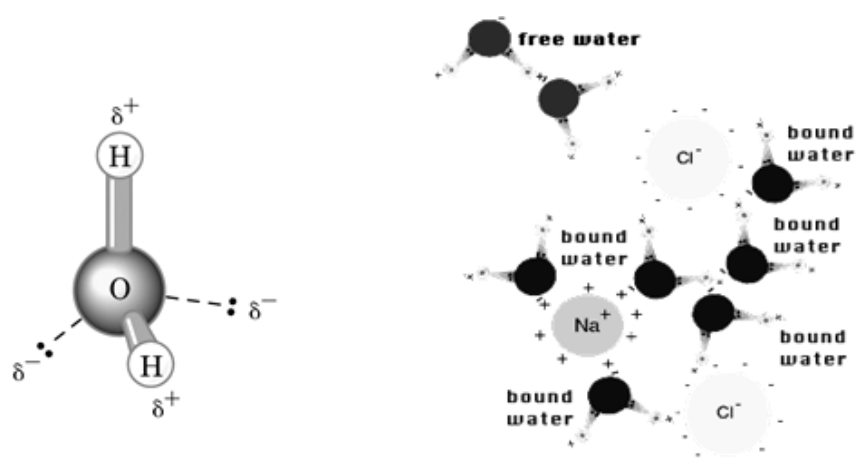


Figure 2.1 Water structure, bound water and free water

Source: www.academic.brooklyn.cuny.edu

According to the interaction between water molecules and food components, water molecules can be divided into 2 types; bound water and free water. Bound water has high bonding energy between water and food components such as ionic or hydrogen bonding. Free water is loosely bound or lower bonding energy than bound water. Amount of free water was used as a tool for predicting food perishable (Botlan, Rugraff, Martin, and Colonna, 1998; Buonocore et al., 2003).

Water activity can be used for describing the energy requirement for breaking water molecules from food products. Water activity is relevant to food quality and

food safety because chemical reaction and microbial growth are stimulated by the increasing of water activity. The water activity measurement of food products requires the experimental data at the equilibrium condition which the partial pressure of food product equilibrated with partial pressure of pure water. Thus water activity (a_w) is defined as the ratio between partial pressure of water above food product (p) to the partial pressure of pure water (p_0) at the same temperature (Labuza, 1985; Hamdami, Monteau and Bail, 2004) as shown in Eq (2.1).

$$a_w = \frac{P}{P_0} \quad (2.1)$$

Fontana and other (2000) described the definition of water activity which investigated from the role of thermodynamics and physicochemical properties. The thermodynamic properties are defined as the chemical potential of system at equilibrium condition at each storage temperature and calculated by Eq. (2.2)

$$\mu = \mu_0 + RT \ln\left(\frac{f}{f_0}\right) \quad (2.2)$$

The chemical potential (μ) is an energy change when increasing the number of particles in the system which related to fugacity of system. The fugacity (f) and f_0 are referred to the escaping of solvent from solute and fugacity of pure water. The difference between P/P_0 and f/f_0 is less than 1 % thus, the activity of material is defined as $a = \frac{f}{f_0}$. Therefore, the partial pressure (P) equals to fugacity of material ($P=f$). According to the relationship between fugacity and partial pressure, water activity of food can be calculated as Eq. (2.3) when the chemical potential of water was equivalent with chemical potential of pure water which demonstrated an

equilibrium condition. Moreover, the water activity has the relation with relative humidity of air, as showed in Eq. (2.4).

$$a_w = \frac{f}{f_0} \cong \frac{P}{P_0} \quad (2.3)$$

$$a_w = \frac{P}{P_0} = \frac{ERH(\%)}{100} \quad (2.4)$$

The water activity relates with storage condition thus its must be control to fit with the particular food type in order to minimize the deterioration rate. The important of water activity in food products are demonstrated in Fig 2.2 which used as a tool for predicting food stability and food safety. The water activity also represents the state of water which significant information to food processing. In addition, it describes the energy state of water in foods products. The rates of chemical reactions including lipid oxidation, Maillard reactions and microbial growth are affected by the water content. Food industries often apply the quantity of water activity for predicting the deterioration rate from enzyme activity and microorganism (Merdeiros, Ayrosa, Pitombo, and Lannes, 2005). For example the quality changes of dehydrated foods are affected by water activity alteration. Domingues and others (2007) studied the effect of water activity on physical and chemical changes of macadamia nut and found that the level of peroxide value was higher at a_w of 0.628 than the ones at a_w 0.2 and 0.4. However, the effect of water activity on food quality depends on product porosity and moisture sorption isotherm behavior (Hamdami et al., 2004).

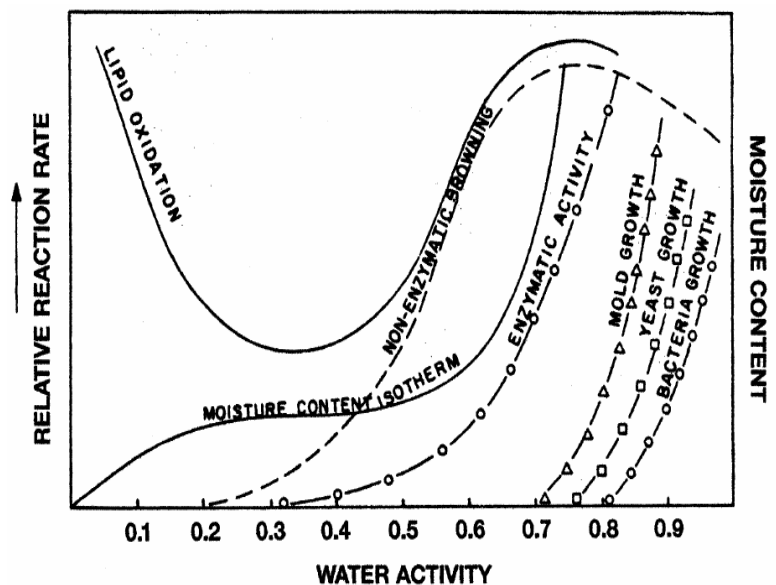


Figure 2.2 Relationship between water activity, moisture content and relative reaction rate in food

Source: Sewald and Devries (2003)

2.1.2 Sorption process

2.1.2.1 Classification of sorption process

Sorption process is the interaction between atoms or molecules on solid surface such as liquid on solid surface (liquid-solid adsorption) and gas absorbed on solid surface (gas-solid adsorption) which some parts of them cannot interact on solid surface (free molecule). In gas-solid adsorption, gas molecules act as absorbate and solid surface as absorbent in sorption system. Sorption process composes of adsorption and desorption. In addition, they can be divided into 2 types which are physisorption and chemisorption (Zola, Greire, Lenzi, Evangelista and Barbero, 2007).

- Physisorption is an interaction between adsorbate and adsorbent molecules with low bonding energy. Physisorption involves the low energy releasing because the process does not influence on electron transfer and need no specific sorption sites.

- Chemisorption is a high energy interaction which adsorbate molecules are tightly absorbed on adsorbent via the chemical bonding and the process involves a higher releasing energy than the physisorption.

Initiation of sorption process is a direct interaction between adsorbate and adsorbent molecules which defined as first sorption layer or monolayer and usually approximate on the basis of 1 mol water to 1 mol of highly polar groups (Fennema, 1985). For the subsequent layers, the adsorbates molecules can react with themselves resulting in multilayer of sorption as shown in Fig 2.3. The water activity of sorption system is measured via partial pressure of water which depends on storage temperature. At the equivalent partial pressure of water between adsorbate-adsorbent and environment was defined as equilibrium condition.

The sorption process of foods is classified as a complex system that has many sorption phenomena. Food products contain numerous compositions such as carbohydrate, protein and fat. These compositions show dissimilar chemical bonding with water molecules. For example, hydrogen bonding of water can occur with various potentially groups such as hydroxyl, amino and carbonyl groups. Moreover, the interaction of water with non-polar substances can also be found with hydrocarbons and apolar groups of fatty acids. However, water interaction in food system is temperature dependence. Therefore, the water activities of various foods are determined at each storage condition which equal to the equilibrium relative humidity of air at the same storage temperature (Arslan and Togrul, 2005).

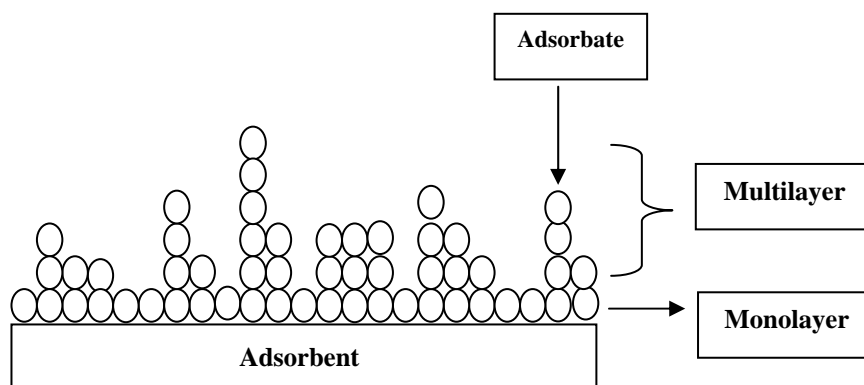


Figure 2.3 Monolayer and multilayer adsorption

Source: Doung (1998)

2.1.2.2 Moisture sorption isotherm

According to the general profiles of moisture sorption as appeared in Fig 2.4, water activity is divided into 2 zones to relate the amount of water with physicochemical changes.

- Low moisture zone (a_w 0 – 0.25) is the direct interaction between water and food which is the highest interaction energy. A water molecule in this region has no movement or is in the state of unfreezable water at $-40\text{ }^\circ\text{C}$ and the enthalpy of vaporization of this water is much greater than that of pure water, thus there is unavailable water for chemical reaction and microbial growth.

- Intermediate moisture zone (a_w 0.25 – 0.75) is consisting of low moisture water plus added water which compose of water-solid and water-water interaction. The multilayer of sorption is occurred due to the additional layers. This moisture zone has lower energy bonding than previous zone. The enthalpy of vaporization for multilayer water is slightly greater than that of pure water. Water molecules are

moveable water therefore, they act as plasticizing agent and solvent for chemical reactions.

- High moisture zone ($a_w > 0.75$) contains a lot of free water because water added in this zone is the least strongly bound and the most mobile water in foods. The enthalpy of vaporization has the same as that of pure water. This moisture zone is freezable water, available for chemical reaction and microbial growth.

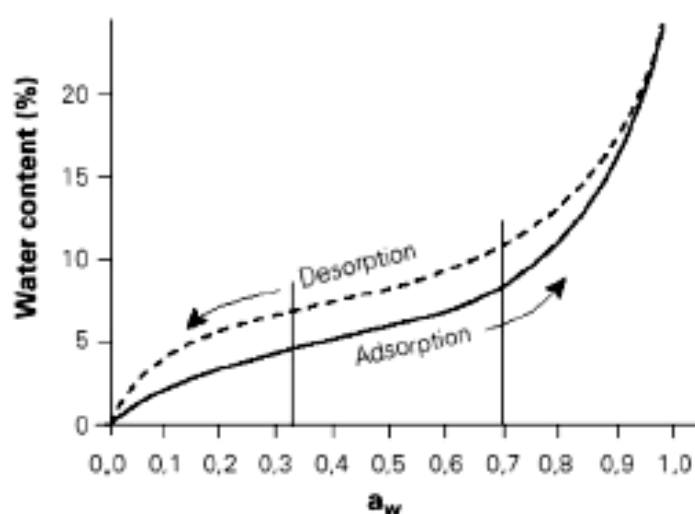


Figure 2.4 Moisture adsorption and desorption isotherm behaviors

Source: Mathlouthi, 2001

Moisture sorption isotherm represents the relationship between the equilibrium moisture content and water activity at constant temperature (Ahmed, Ramswamy, and Khan, 2005) as seen in Fig 2.4. Moisture sorption isotherm is divided into adsorption and desorption isotherms. These processes are temperature dependent according with water activity. The knowledge base of moisture adsorption and desorption behaviors are useful for production design such as drying process, selecting an appropriate equipment and packaging material and predicting in shelf life stability during storage and transportation (Kaymak-Ertekin and Gedik, 2004; Chowdhury, Huda, Hossain,

and Hassan, 2005; Samapundo et al., 2007; Tunc, and Duman, 2007). In addition, sorption data are not only directly used for estimation of moisture changing but physical and chemical changes during storage also indirect prediction. The ability to predict the moisture content during storage under a variety of conditions was shown important for reducing cost and cycle time of process development (Tunc et al., 2007).

Most of food deterioration is taken an effect of moisture changes. In case of low moisture foods are stored at high moisture condition as consequence moisture gaining results in textural changes such as loss of hardness or crispiness for dry food products. The appropriate storage conditions for intermediate and high moisture foods must be considered because moisture loss might occur at low moisture storage condition. Moreover, microbial growth is an important controlled factor due to more movement water is available for many spoilage microorganisms.

The adsorption and desorption isotherms are usually studied in hygroscopic materials due to they absorb more moisture and straightforward to flavor and textural changes. Food products are complex system because they contain more components and have many production methods as a result sorption mechanism is difficult for accurate describing. Further more, the adsorption and desorption are unusual behaviors due to difference amount of bonding and bond strength (Samapundo, et. al, 2007). Both of adsorption and desorption are essential to food products, the adsorption is needed for dry food while desorption is significant to intermediate and high moisture foods. Brunauer and others studied food and their components isotherms and divided into 5 isotherm types as shown in Fig 2.5. Most of food isotherms represent type II isotherm or sigmoid shape such as cookies, snack, corn,

peanut and fruits (Palou, Lopez-Malo, and Argai, 1996; Chowdhury et al., 2005; Kaymak-Ertekin et al., 2004).

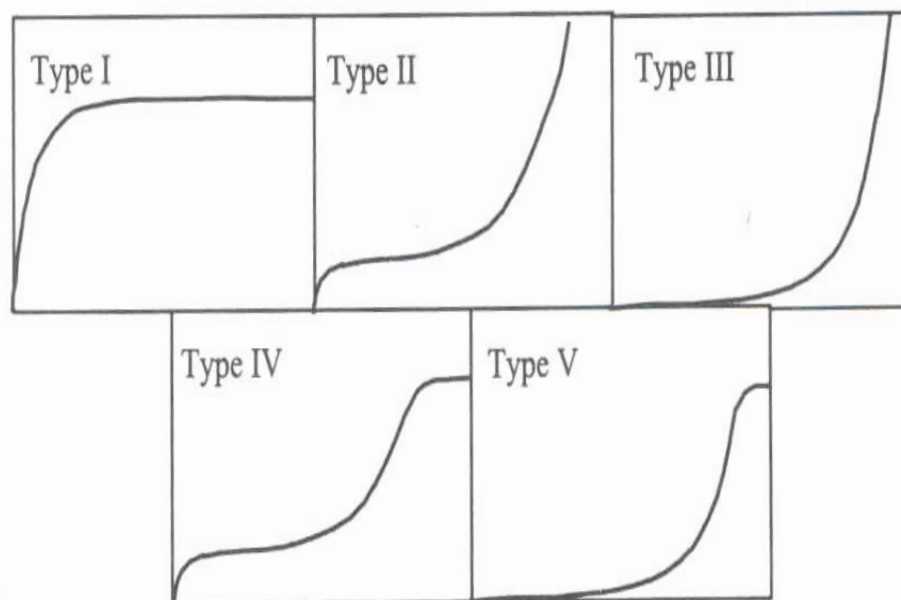


Figure 2.5 Isotherm types of materials

Source: Duong (1998)

Hysteresis effect represents the difference of equilibrium moisture content between adsorption and desorption process. Desorption curve also lies above adsorption curve but this behavior is not found for all food products. The magnitude of hysteresis depends on food type and storage temperature, it increases with increasing temperature. The extent of hysteresis can be used for estimating the possibility of deterioration by chemical reaction and microorganism (Aviara, 2005; Sander, Lu and Pignatello, 2005; Frankowicz and Chrenowski, 2006).

2.1.3 Mathematical model for moisture sorption isotherms

Several mathematical models were derived for describing the moisture adsorption and desorption isotherms of various types of foods, since the numerous of

components and complexity of food interaction play an important role on moisture sorption phenomenon. Many mathematical models are proposed in literature such as system energy model on monolayer and multilayer of sorption semi-empirical and empirical equations (Siripatrawan, and Jantawat, 2006; Peng, Chen, Wu, and Jiang, 2007). Mathematical expressions for adsorption and desorption isotherms are summarized in regards of various existing models as shown in Table 2.1. New mathematical models are still-researched to obtain a better describing tool for all class of solid food and products. The model constant is involved with the basis of model development including Brunauer, Emmett & Teller (BET) model. Constant C is temperature dependent and corresponding to surface coverage of adsorption affecting on adsorption rate. For the parameter of Guggenheim-Anderson-de Boer (GAB) model, M_0 is related to monolayer moisture content while C is developed base on state of adsorbed molecule which relate by means of volume and interaction between adsorbate and adsorbent molecules and constant K is occupied for properties of water molecule at multilayer of sorption (Das and Das 2002; Vazquez, Chenlo, and Moreira, 2003). Most of mathematical models contain two and three constants which each constant model is occupied the physical state or chemical reaction of sorption behaviors (Adolphs and Setzer, 1996; Arslan et al., 2005). All models can be selected for describing the moisture sorption isotherm of various foods including Halsey and Oswin models which fitted well with the experimental data of chickpeas flour, dehydrated tomato. The Halsey model provides a satisfactory for sorption isotherm of withered leaves, black and green tea (Durakova, 2004; Akanbi, 2006 and Ghodake, Goswami, and Chakraverty, 2007). BET model usually provides sorption isotherm behavior and predicting of equilibrium moisture content at the first sorption layer or

monolayer moisture region. BET model was found to fit with the experimental isotherm of pepper at a_w 0.1- 0.5 and also satisfied for moisture sorption isotherm of safflower petals and tarragon at a_w 0.06-0.52 (Kaymak-Ertekin, 2001 and Kaya, 2007). GAB model always used for moisture content for prediction the whole range of water activity including cocoa, corn starch, almond and oat isotherm (Medeiros, 2005; Peng, 2007; Pahlevanzadeh, 2004; McMinn, Al-Muhtaseb, Magee, 2005).

Table 2.1 Mathematical models for describe moisture adsorption and desorption isotherm behaviors

Model	Equation
BET (Brunauer, Emmett & Teller, 1938)	$M = \frac{M_o c a_w}{[(1 - a_w) + (c - 1)(1 - a_w) a_w]}$
GAB (Guggenheim-Anderson-de Boer) (Van den Berg, 1985)	$M = \frac{M_o C K a_w}{[(1 - K a_w)(1 - K a_w + C K a_w)]}$
	$C = C_o \exp(\Delta H_c / RT)$
	$K = K_o \exp(\Delta H_k / RT)$
Chung-Pfost (Chung & Pfost 1967)	$a_w = \exp[-k / RT \exp(-cM)]$
Halsey (Halsey, 1948)	$a_w = \exp[-k / M^n]$
Henderson (Henderson, 1952)	$1 - a_w = \exp(-kTM^n)$
Oswin (Oswin, 1946)	$M = k(a_w / 1 - a_w)^n$

Source: Kaymak-Ertekin et al., (2004)

2.1.4 Thermodynamic properties of adsorption and desorption isotherms

Even through moisture sorption isotherm cannot be used directly as an indicator for determination the chemical reaction rate, the thermodynamics of moisture sorption

process are useful for estimating the moisture sorption rate and the type of food-water interaction. The kinetic rate of moisture sorption is important to food processing in term of controlling the operation to obtain the final moisture content of product and evaluating final requirement that involved in the food processing (Gabas, Telis, Sobral, and Telis-Tomero, 2007). The enthalpy and entropy changes are the important thermodynamic properties which demonstrate the state of water in food at any water activity and environmental conditions. The understanding in thermodynamic properties such as isosteric heat of sorption (differential enthalpy), entropy of sorption give an information for predicting physical and chemical sorption behaviors of various food types. The isosteric heat of sorption is the only one thermodynamic property exhibited the energy relation between water-food surfaces that used as a tool for drying process (Beristain, Garcia, and Azuara, 1996). The entropy of sorption demonstrates the quantity of sorption site that represent the physical state of food surface and their porosity. All thermodynamic characteristics are useful for selecting appropriated packaging material to maintaining flavor, taste and nutrition of food products (Kaya and Kahyaoglu, 2005; Ariaahu, Kaze and Achem, 2006).

Thus, understanding the action of absorbate and absorbent is important for processing mechanism prediction including dissolution, crystallization and swelling (Tunc et al., 2007). The isosteric heat of sorption or differential enthalpy gives the energy requirement for drying process and state of water at each water activity, this value is applied as direct measurement for the adsorption strength (Yazdani, Sazandehchi, Azizi, and Ghobadi, 2006).

2.2 Lipid oxidation

Lipid oxidation is a major problem for all food products specifically high fat-containing foods at the reaction causes an adverse effect on product stability due to a series of organic chemical processes by peroxidation (Angelo, 1991). Amount and degree of unsaturated fatty acid are the most important factors which affecting lipid oxidation (Lampi, Piironen, Hopia and Koivisoinen, 1997; Abou-Charbia, shehata, and Shahidi, 2000; Ansorena, and Astiasaran, 2004; Muik, Lendl, Molina-Diaz and Ayora-Canada, 2005). Lipid oxidation causes major chemical and physical changes including flavor, nutritional, textural and overall appearances. The external factors involved in the lipid oxidation are light, temperature, metal ion and microorganism. The latter two factors act as catalysis for the lipid oxidation, thus, a rate of deterioration is increased. Lipid oxidation may occur in various processes, for example, raw material handling, washing, post processing step, storage and transportation.

Therefore, antioxidants are often added into food products for controlling the lipid oxidation and both natural and synthetic form of antioxidants may be applied depending on the type of foods including α -tocopherol (Vitamin E), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate etc. The inhibitory effect of antioxidant is indeed up to the antioxidant type, level of usage and food system. In addition, some type of antioxidant might be interfering with the product flavor and several type of synthetic antioxidants are classified as food additive, designing the antioxidant system must be abided by the legal limit of usage.

2.2.1 Mechanism of lipid oxidation

Chemical interaction among food components, physical change during food processing and storage conditions are the cause of lipid oxidation in food, resulting in rancidity or off-odor especially in meat and dry food products. Lipid oxidation is always found in fat – containing foods, the degree of reaction depend on type of fatty acids. Unsaturated fatty acids are more susceptible for lipid oxidation than saturated fatty acids. Moreover, degree of unsaturation also affects lipid oxidation. Polyunsaturated fatty acid such as oleic (C_{18:1}), linoleic(C_{18:2}), and linolenic(C_{18:3}) are easily oxidized than monounsaturated fatty acid. The polyunsaturated fatty acids are the main cause of oxidation and generate off-odor.

The oxidation reactions are commonly divided into 3 steps. Firstly an initiation step, oxygen molecules interact with C-atom which form double bond of unsaturated fatty acid as a result free radicals is produced. This step is catalyzed by high temperature, exposure to light, present of high energy free radical as metal ion. Secondly in propagation step, free radicals react with oxygen molecules to form peroxy radicals which can further react with other fatty acid, amino side chains of protein (Nam, 2003). As a result of this step, the amounts of hydroperoxides and free radical products are generated and ready to act as an oxidizing agent for various kinds of reactions. Thirdly termination step can occur from the reaction among free radical molecules and hydroxyl radical which converted to non-radical products. The unstable hydroperoxides are decomposed by scission at oxygen-oxygen bond, providing an alkoxy radical and hydroxyl radical then the C-C bond is cleavage. In general, the cleavages on acid side chain result in formation of an aldehyde and acid

(Fennema, 1985). The formations of aldehydes almost respond to off-odor or rancidity serving for food deterioration.

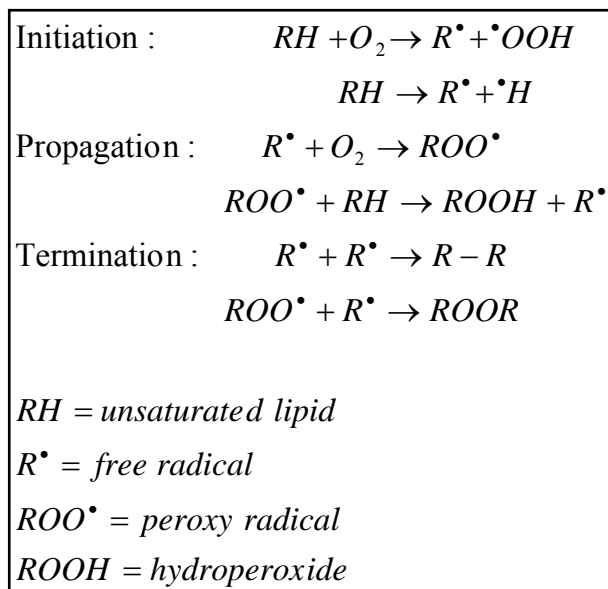


Figure 2.6 Mechanism of lipid oxidation

Source: Angelo (1991)

Lipid oxidation products are achieved in most of flavor change which separated into primary and secondary products. Hydroperoxides are primary product which they are flavorless and tasteless (Gladovic, Aupancic-Kralj and Plavec, 1997). In addition, hydroperoxides are instable products at high temperature thus they are decomposed into secondary products including aldehyde, ketone and alcohols which affecting to flavor alteration (Wanasundara, Shahidi, and Jablonski, 1995). As the fat-containing foods contain monounsaturated and polyunsaturated fatty acids they are oxidized into secondary product through chemical reaction (auto-oxidation) or enzymatic reaction (Montel, Massun and Talon, 1998). For example, autoxidation of linolate produce conjugated hydroperoxides as 9-hydroperoxide would create nonanal, methyl-9-oxononate, 2-decenal and methyl octanoate, 12-hydroperoxide

and consequently give hexanal, methyl-12-oxo-9-dodecenoate, 2-heptanal and methyl-9-undecenoate. The possible origin of aldehydes from the oxidation of oleic, linoleic, linolenic and arachidonic acid are shown in Table 2.2. Thus assessment of oxidation products can be measured via both of primary and secondary products depending on food types and their shelf-life.

Table 2.2 Possible origin of aldehydes obtained from the oxidation of oleic, linoleic and linolenic

Fatty acid	Hydroxide Position	Aldehyde Obtained
Oleic	C11	Octanal
	C8	2-undecenal
	C9	2-decenal
	C10	Nonanal
Linoleic	C13	Hexanal
	C9	2,4-decadienal
	C11	2-octenal
Linolenic	C16	Propanal
	C14	2-pentenal
	C12	2,4-heptadienal
	C13	3-hexanal
	C11	2,5-octadienal
	C9	2,4,7-decatrinal

Source: Shipe (1980)

2.2.2 Determination of lipid oxidation

Many analytical methods for lipid oxidation are developed for an accurate determination dividing into primary and secondary product measurement. For example, peroxide value and oxygen consumption are used as analytical method for tracking a primary oxidation product. Lipid peroxides are found during processing

and storage which initially cause food deterioration and diseases (Goupy, Vulcain, Caris-Veyrat, and Dangles, 2007). Calligaris and Nicoli (2006) studied the effect of metal ion on lipid oxidation in soy oil and the extent of oxidation by measuring the number of hydroperoxide and hexanal, the result demonstrated that peroxide values gradually increased at initiation then, decreased while hexanal contents increased throughout storage time. This is due to the fact that hydroperoxides usually breakdown into aliphatic aldehydes that take effect on product off-flavors. As the instability of hydroperoxides, analytical methods for primary products are inappropriate for predicting lipid oxidation over storage time.

In general, the secondary products are used for marker of lipid oxidation rather than primary products because they can be determined throughout storage time for the most part of long shelf life foods such as dry food products. Many analytical methods are proposed for secondary products such as thiobarbituric acid reactive substances (TBARS), volatile compounds analysis by Gas chromatography (GC), Mass spectrophotometry – gas chromatography (GC-MS) and other methods (Jensen, Danielsen, Bertelsen, Skibsted, and Andersen, 2005). In addition, TBARS is a typical method for lipid oxidation measurement which measure via the chemical reaction between malonaldehyde (MDA) and Thiobabituric acid (TBA) (Fig. 2.7). TBARS color reaction is generated through the reaction between MDA reacts with two molecules of TBA and measured by UV- visible light at appropriate wavelength (Campo, 2006). However, the MDA reaction might be interfered with various compounds producing red pigment or conjunction with TBA upon reaction of MDA analysis including alkenal, alkanal and 2, 4-dienals which can react with TBA reagent resulting in yellow pigment. The amount of MDA depends on production method,

storage time and temperature. The MDA content in food products should be concerned due to its carcinogenicity.

Statistic headspace gas chromatography is one of analytical methods for lipid oxidation measurement with high efficiency for volatile compounds because most of them are exist in gas phase and small amount of sample is required for analysis. Aldehydes are a group of volatile compounds that commonly found in oxidation of food products such as octanal, nonanal, pentanal and hexanal (Ross and smith, 2006). The hexanal is frequently used for rancidity index and easier detected than other volatile compounds. However, the off-flavor compounds are not only generated by lipid oxidation but might be occurred from protein degradation by deamination and decarboxylation of amino acids by α -dicarbonyl compounds.

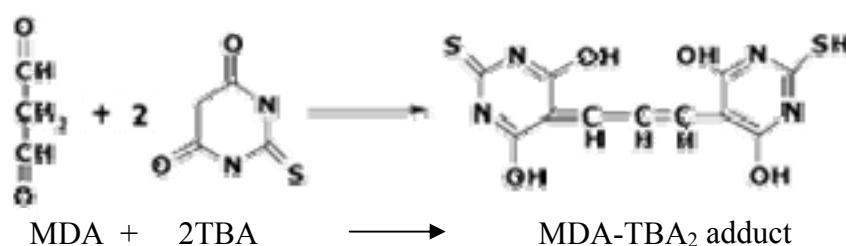


Figure 2.7 Reaction of malonaldehyde (MDA) with thiobarbituric acid forming MDA-TBA₂ adduct

Source: Fernandez, Perez-Alvarez and Fernandez-Lopez, (1997)

2.2.3 Inhibition of lipid oxidation

Lipid oxidation can be inhibited or delay by control of storage conditions such as maintaining low storage temperature and store under dark condition. Nevertheless, only controlling in storage condition is insufficient for inhibiting lipid reaction thus researchers attempt to find new additive substances for food preservation.

Preservative substances for hindering lipid oxidation or antioxidant are divided into 2 types there are natural antioxidant e.g. δ -tocopherol (vitamin E), ascorbic acid (vitamin C) and synthetic antioxidant e.g. Butylated hydroxyanisole (BHA), Butylated hydroxytoluene (BHT), and tertiary butylhydroquinone (TBHQ) as shown in Fig 2.8. The natural antioxidant can be extracted from various food materials including grape fruit seed extract, wheat bran, onion and garlic (Armando, Maythe, and Beatriz, 1998; Kim, Tsao, Yang, and Cui, 2006; Moreno, Corzo-Martinez, Dolores del Castillo, and Villamiel, 2006). At present, natural and artificial antioxidants are used in food industries to preserve stability, quality, nutrition and shelf life of foods. Natural antioxidants are used as food preservative in healthy foods due to the benefit and less hazard for consumer healthiness than synthetic antioxidant. The synthetic antioxidants are usually added into feedstuff including shrimp meal to serve stability and less economic loosen (Bautista-Teruel and Subosa, 1999). BHA and BHT are antioxidants mostly used in food products which decrease the reaction ability between radical and fatty acid peroxy radical (Khan and Shahidi, 2001).

In addition, antioxidants can be separated by functional properties into 2 types, there are primary or chain breaking antioxidant and secondary or synergist antioxidant. Primary antioxidants are terminating of radical chain reaction by acting as hydrogen or electron donors to free radical resulting in the formation of stable compounds. Secondary or synergists antioxidants are acting as oxygen scavenger, chelating complex with pro-oxidant and decompose the lipid peroxides into stable products. BHA and BHT are phenolic antioxidants are mainly used as food preservative which more effective providing the oxidative stability in model system of lean muscle and canola oil (Raghavan and Hultin, 2005). The antioxidant properties

of BHA and BHT was tested by refluxing in ferric chloride solution and showed stronger antioxidant in lard which gave longer induction period than other antioxidants (Duan et al., 1997). Phenolic antioxidants inhibit the oxidation of lipid, fat and proteins by donating of phenolic hydrogen atom to chain-carrying peroxy radical (ROO[•]). The stereoelectronic effects of phenol and phenoxyradical are greatly responsible for their reactivity with peroxy radical (Nicolik, 2006). Conversely, the adverse effects of synthetic antioxidant are found, thus doses of antioxidants added are controlled or decreased by mixing with the same group or with natural antioxidants. Mixing of two antioxidants demonstrates the synergistic antioxidants and illustrates high antioxidant activity including mixing between oxygen scavenger and chelator antioxidants, they will be react with metal ion resulting in complexity and more stable compounds. The effect of synthetic antioxidants on storage stability of semi-solid concentrated milk products were studied and revealed that sample added BHA along with BHT had higher antioxidants activity (low peroxide value and free fatty acid) than only added BHA or BHT alone (Rehman and Salariya, 2006)

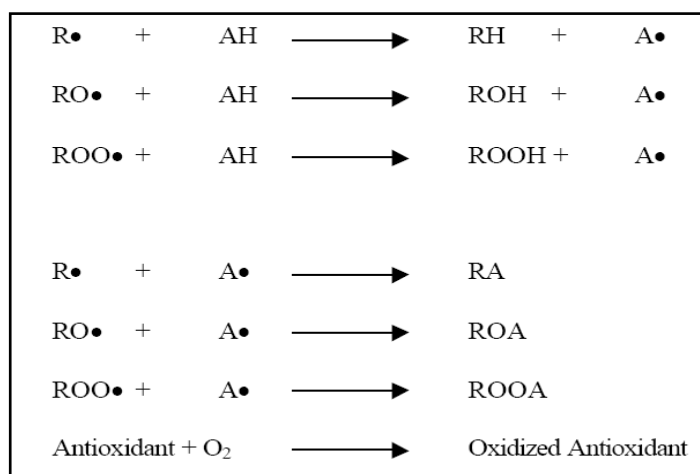


Figure 2.8 Mechanism of antioxidant to inhibit lipid oxidation

Source: Farhoosh (2005)

Synthetic antioxidants (BHA and BHT) are still used in food products, although they have adverse effect on healthiness (Osada and Shibamoto, 2006) due to cheaper and high antioxidant activity. BHA and BHT demonstrated higher antioxidant activity in benzoyl peroxide system than natural antioxidant as α -tocopherol (Fugisawa and Kadoma, 2003). Bautista-Teruel and others (1999) studied the effect of BHT on shrimp growth and found higher growth rate in feed with BHT than feed without BHT and adverse effects were not found. In this case, the synthetic antioxidants also were added in the food with the level limited by FDA (Food and Drug Administration) and AAFCO (The association of American Feed Control Officials).

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CHAPTER III

MOISTURE ADSORPTION AND DESORPTION

ISOTHERMS OF DRY FOOD MODELS

3.1 Abstract

Moisture adsorption and desorption isotherms of dry food models were investigated at 25, 35, and 45 °C using static gravimetric. Dry food models in this research were covered for dry food model A and B which have different in protein source. Besides they divided for normal dry food and contained high protein and fat content foods. The moisture sorption isotherms for all dry food models were classified as a type II (S-shape) isotherm. The effect of high protein and fat content was not found both types of dry food models. The equilibrium moisture content of all dry food models studied was decreased with increasing temperature at constant water activity. The hysteresis of sorption was clearly identified for the storage temperature of 25 and 35 °C. Five mathematical models (BET, GAB, Oswin, Halsey, and Chung&Pfoest) were tested against the experimental data. GAB model was the best suitable model for describing moisture sorption isotherm behaviors. BET model was selected for monolayer moisture content (M_0) calculation, M_0 of all dry food models studied were demonstrated temperature independent. Isothermic heat and entropy of sorption were demonstrated a decreasing function of moisture content which found for every testing sample of all dry food models studied.

Keyword: Dry food, Sorption isotherm, Hysteresis, Thermodynamic properties

3.2 Introduction

Dry food products are most important due to convenience, high nutritious, health care and long shelf life stability. Cereals, meat, poultry meals, are commonly ingredients for dry food production. Dry food industries are developing at a continuous for producing specific dry food products. The problems of dry food products were occurred such as flavor and textural alterations at the period of storage and distribution. Therefore, understandings in transformation factors are important for prediction changing level at various storage conditions such as different temperature and moisture.

Moisture adsorption and desorption isotherms corresponding to relationship between equilibrium moisture content per unit dry mass and water activity or relative humidity at constant temperature (Arslan and Togrul, 2005). Water activity indicates the state of water in food which represents amount of water binding and availability to participate into physical and chemical reactions (Al-Muhtaseb, McMinn, and Magee, 2004). Moisture sorption isotherm behavior of food products depend on their composition, processing and storage condition. The effect of temperature is most important factor which influence on moisture sorption isotherm caused by affecting to water activity of air and moisture content of food products. The water gradients are affecting to moisture content of food product which the mobility greatly depends on temperature system.

Moreover, Most of dry foods are extruded products which expansion process resulting in more porosity and amount of sorption surface thus expansion have a directly effect on equilibrium moisture content. The porosity involves with water diffusion rate or water migration in food combine with the effect of temperature and

water migration which critical to quality and food safety for the most part of dehydrated foods (Al-Muhtaseb et al., 2004; Guillard, et al., 2004; Roca, Guillard, Guilbert, and Gontard, 2005). Many analytical methods are used for moisture sorption isotherm determination including manometric and gravimetric techniques but this method is preferred for complete moisture sorption isotherm determination (Aviara, Ajibola and Oni, 2004).

In general, a hysteresis phenomenon was found in moisture sorption isotherm of various food materials. This phenomenon usually occurs in solid sorbent system caused by the different equilibrium moisture content between adsorption and desorption processes which desorption isotherm always lies above adsorption isotherm (Kaleemullah and Kailappan, 2004). The hysteresis effect is significant to sorption isotherm which the magnitude of hysteresis influences on natural and state of food components which take an effect on textural of their food products. However, the hysteresis might be reduced by drying cycle. The definition of hysteresis for food products can not an accuracy identify due to complexity of food and contain many type of relations between water – food component or water-water interactions.

Model expressions for moisture sorption isotherm are valuable for describing sorption isotherm behavior at each water activity. Sorption model was used as primary information for design preservation process such as estimating in drying time, shelf-life stability in various packaging material and storage conditions. Moisture sorption models were recommended in literature which can divide for kinetic model base on monolayer (BET model), kinetic model base on multilayer (GAB model), semi-empirical model (Handerson and Halsey) and empirical model (Smith and Oswin) (Gabas, Telis, Sobral, and Telis-Romero, 2007; Kaya and Kahyaoglu, 2007).

The GAB (Guggenheim Anderson DeBoer) model has been recommended for describing moisture sorption isotherm of dehydrated foods which this model was developed base on BET model and contained three model constants which have a meaningful to physical changes and two model constants are function of temperature (Telis, Gabas, Menegalli, and Telis-Romero, 2000).

Thermodynamic properties of moisture sorption isotherm are investigated due to relate with enthalpy-entropy compensation of sorption process and refer to physical and chemical interaction between water and food components. The thermodynamic of sorption including differential enthalpy (isosteric heat), differential entropy, integral enthalpy, and integral entropy and spreading pressure are useful for food processing (Al-Muhtaseb et al., 2004). These properties give the information of sorption process and involve with properties of water, food microstructure, and physical phenomena on food surface (Kaya and Kahyaoglu, 2005). The differential enthalpy or isosteric heat of sorption were provided the state of water even as absorbed on solid sorbents and used as equipment for predicting the energy requirement for drying or other dehydration processes. Besides that isosteric heat of sorption is greater than latent heat of vaporization of pure water at particular temperature as the indicative for high intermolecular attraction force between water and sorption sites (Goula, Karapantsios, Achilias, and Adamopoulos, 2007; Simal, Fernenia, Castell-Palou and Rossello, 2007). The differential entropy describes for quantity and quality in term order/disorder of absorbed molecules or related to number of available sorption sites at specific energy level (Perez-Alonso, Beristain, Lobato-Calleros, Rodriguea-Huezo, and Vernon-Carter, 2006; Dominguez, Azuara, Vernon-Carter, Beristain, 2007; Al-Mahasneh, Tababah and Yang, 2007).

The knowledge of absorption and desorption behaviors of dry food product can predict for the physical and chemical changes during storage at different storage conditions and distributions. Furthermore sorption isotherm data can apply for thermodynamic properties calculation which valuable for processing design, suitable packaging material selection and predicting in state of water exiting in food products.

3.3 Material and method

3.3.1 Materials

Dry food models in this research compose of dry food models A and B which have a different protein source. Besides they were divided for normal product and product contained high protein and fat content. All dry food products were brought from Thai market, both of dry food models A and B have initial moisture content about 7.5 % (dry basis) and the other proximate analysis showed in Table. 3.1.

Table 3.1 Proximate compositions of all tested samples

Type*	Proximate analysis (%)			
	Protein	Fat	Fiber	Moisture
Model A-H	26.00	12.00	5.00	7.50
Model A	18.00	10.00	5.00	7.50
Model B-H	30.00	12.00	4.50	7.50
Model B	26.00	10.00	5.00	7.50

*H = High protein and fat content

3.3.2 Sample preparation

Samples had been stored at 4 °C until needed for the isotherm experiment. For adsorption isotherm, samples 2-3 g were weighted onto aluminium dishes and pre-dried in a vacuum oven at 70 °C for 24 hrs (Leuschner, O'Callaghan, and Arendt, 1999). Initial moisture content of dry food models were obtained from this step. For desorption isotherm, triplicate samples (2 -3 g) were placed onto aluminium dishes and moisture added by placing in a humidity chamber with 80-90 % relative humidity at 25 °C for 4-5 days. The initial moisture content was determined by AOAC 1990 method. All experiments were done in triplicate and moisture contents were express as percentage of dry basis.

3.3.3 Saturated salt solution preparation

Eight analytical grade salts were used for specific water activity making, there were LiCl, CH₃COOK, MgCl₂, K₂CO₃, NaNO₂, NaCl, (NH₄)₂SO₄, and KNO₃. All analytical salts were generated water activity ranges 0.12 – 0.92 as seen in table 3.2. Salt crystals were dissolved in distilled water at 45 °C until reach saturation and excess salt crystals were added to saturated salt solutions to ensure that saturated condition was maintained throughout the experimental time. The saturated salt solutions were placed into moisture sorption isotherm containers and put on the temperature control chamber which were set at the temperature of 25, 35 and 45 °C (HOTPACK, 175 Series). Relative humidity of all saturated salt solutions were measured using humidity sensor (Dataloger testo 175 (-20 °C to +70 °C)) and the level of relative humidity in the moisture sorption isotherm (MSI) container is constantly monitored till the end of experimental time.

Table 3.2 Water activity of air generated by saturated salt solutions

Salt	Water activity (a_w) [*]		
	25 °C	35 °C	45 °C
LiCl	0.12	0.12	0.14
CH ₃ COOK	0.22	0.22	0.24
MgCl ₂	0.35	0.33	0.35
K ₂ CO ₃	0.44	0.41	0.44
NaNO ₂	0.66	0.60	0.66
NaCl	0.73	0.73	0.73
(NH ₄) ₂ SO ₄	0.79	0.78	0.79
KNO ₃	0.92	0.90	0.89

* The value is an average and the error of humidity sensor is declared within the range of $\pm 3\%$ RH

3.3.4 Determination of moisture adsorption and desorption isotherms

Moisture adsorption and desorption isotherms were determined by gravimetric method at the temperature of 25, 35 and 45 °C. The equipment for moisture sorption isotherm determination composes of air tight plastic container equipped with saturated salt solution and temperature control chamber. Sample dishes were placed onto moisture sorption isotherm container which each container has constant water activity. Five milliliters of toluene was added to prevent fungal growth and all of MSI containers were kept into the temperature control chambers. Samples were weighed at time interval until weight change less than ± 0.001 g. At the end of experimental time, all samples were weighed and the equilibrium moisture content for all samples were determined by the method of AOAC (1990) and equilibrium moisture content was calculated as Eq. (3.1)

$$MC(dry\ basis) = \frac{W_e - W_d}{W_d} \quad (3.1)$$

where; W_e = Sample weight at equilibrium condition

W_d = Sample weight at equilibrium after drying

3.3.5 Mathematical expression for moisture adsorption and desorption isotherm

Five isotherm models consist of BET (Brunauer-Emmett-Teller), GAB (Guggenheim-Anderson-deBoer), Oswin, Halsey and Chung & Pfoest models were selected to fit with the experimental data which showed as in Table 3.2. These models are most widely applied to explain moisture sorption isotherm behavior of various foodstuffs. The model constants were estimated using a non-linear regression analysis. BET model was used for describing the moisture sorption isotherm at monolayer moisture content (a_w 0 -0.5). The best suitable model was evaluated by mean relative error (MRE), regression coefficient (R^2), standard error of estimate (SEE), and residual sum of squares (RSS) which calculated as Eq. 3.2 – 3.5 (Menkov, Durakova and Krasteva, 2004; Chowdhury, Huda, Hossain, and Hassan, 2005; Yazdani, et al., 2006; Peng, Chen, Wu, and Jiang, 2007; Ghodake, Goswami, and Chakraverty, 2007).

$$MRE = \frac{100}{N} \sum \left| \frac{M_e - M_p}{M_e} \right| \quad (3.2)$$

$$R^2 = \frac{\sum (M_e - M_p)^2}{\sum M_e^2 \sum M_p^2} \quad (3.3)$$

$$SEE = \sqrt{\frac{\sum (M_e - M_p)^2}{df}} \quad (3.4)$$

$$RSS = \frac{\sum (M_e - M_p)^2}{N} \quad (3.5)$$

Table 3.3 Mathematical expressions for moisture adsorption and desorption isotherms of dry pet foods

Model	Equations
BET(Brunauer-Emmett-Teller) (1983)	$M = m_0 C a_w / [(1 - a_w)(1 + (C - 1)a_w)]$ (3.6)
GAB(Guggenheim-Anderson- deBoer)(1985)	$M = \frac{m_0 C K a_w}{[(1 - K a_w)(1 - K a_w + C K a_w)]}$ (3.7)
Oswin (1946)	$M = k(a_w / 1 - a_w)^n$ (3.8)
Halsey (1948)	$M = \left(\frac{-a}{\ln(a_w)} \right)^{\frac{1}{r}}$ (3.9)
Chung and Pfof (1967)	$M = a + b \ln(-\ln a_w)$ (3.10)

3.3.6 Thermodynamic properties

Differential enthalpy or isosteric heat of sorption and differential entropy were selected for calculating thermodynamic properties of dry food models.

3.3.6.1 Isosteric heat of sorption (ΔH)

Isosteric heat of sorption represents the binding energy of absorbed water on food surfaces (Perez-Alonso et al., 2006) or demonstrates the latent heat difference between the latent heat of adsorption and condensation of pure water (Kaya and

Kahyaoglu, 1998). The isosteric heat of sorption can be estimated using the van't Hoff equation, the Gibbs-Helmholtz and the Gibbs free energy as follows:

$$\frac{\Delta H}{RT^2} = - \left[\frac{\partial \ln a_w}{\partial T} \right]_m \quad (3.11)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (3.12)$$

$$\Delta G^0 = -RT \ln a_w \quad (3.13)$$

$$\ln a_w = - \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad (3.14)$$

The isosteric heat of sorption (ΔH) was determined by a slope of the linear equation (3.14).

3.3.6.2 Differential entropy (ΔS)

The entropy change relates to a number of available sorption sites at specific level (Al-Muhtaseb et al., 2004; Kaya et al., 2005). The differential entropy was determined by Eq. (3.14) which considered varying only to a_w but not for a temperature set point.

3.4 Results and discussion

3.4.1 Moisture adsorption and desorption isotherms

3.4.1.1 Moisture adsorption and desorption isotherm of dry food

model A and A-H

Moisture adsorption and desorption isotherms of dry food model A-H and A at the temperature of 25, 35 and 45 °C were demonstrated in Fig. 3.1 -3.2 for model A-H and A, respectively. The equilibrium moisture content (EMC) at each water activity represents the mean value of three replications. Both adsorption and desorption

isotherms of the dry food model A-H and A were classified as the type II isotherm or S-shape which was a similar pattern for many food types, for instance, flour of popped, malt sorghum, and starch food (Laseken and Laseken 2000; McMin, McKee, Ronald, and Magee, 2007). The EMC increased as a function of product water activity or relative humidity of surround air at any constant temperature, but the EMC decreased with an increase in temperature at constant water activity. At high water activity, the sorption site of the extrude product was increased as a result of product swelling. The difference EMC between adsorption and desorption isotherms demonstrated hysteresis phenomenon. Hysteresis effect was found for both of dry food model A-H and A. However, the hysteresis were clearly identified for the sample groups incubated at 25 and 35 °C, but the magnitude of hysteresis was drastically decreased for the ones stored at 45 °C. The hysteresis might be a consequence of an irreversible process of physico-chemical changes during dehydration (Vazquea, Chenlo, and Moreica, 2003; Arslan et al., 2005). Low hysteresis magnitude, found at high temperature was due to a high energy level of absorbed water molecules. These molecules were broken away from sorption sites when compared with low energy molecules (Aviara, Ajibola, Aregbesola, and Adedeji, 2006; Tarigan, Prateepchaikul, Yamsaengsung, Sirichote, and Tekasakul, 2006).

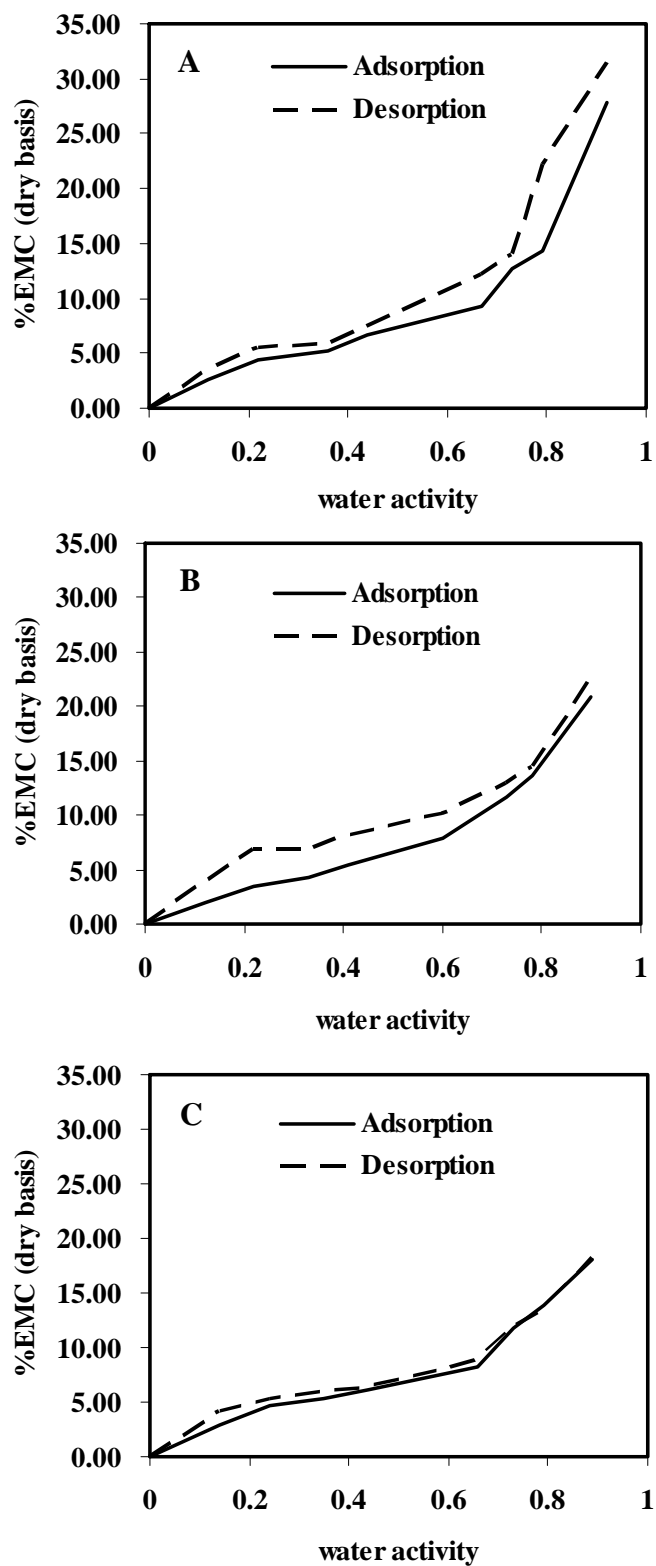


Figure 3.1 Adsorption and desorption isotherms of dry food model A-H at (A) 25,(B) 35 and (C) 45 °C

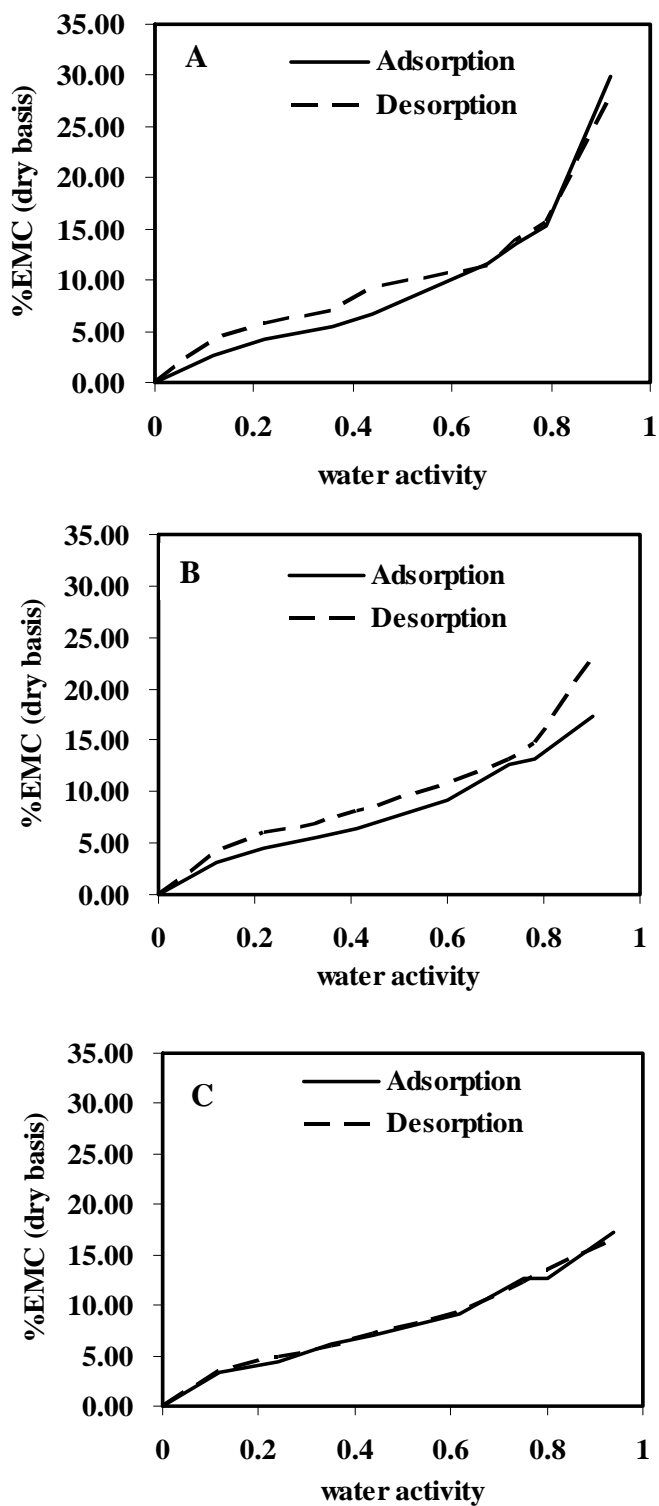


Figure 3.2 Adsorption and desorption isotherm of dry food model A at (A) 25, (B) 35 and (C) 45 °C

3.4.1.2 Moisture adsorption and desorption isotherms of dry food model B and B-H

Moisture adsorption and desorption isotherms of dry food models B-H and B were represented as in Fig. 3.3 -3.4, respectively. Moisture adsorption and desorption isotherms of all dry food models B were also followed the type II isotherm. Hysteresis phenomenon of all dry food models B were obviously found for all temperature studied. High storage temperature, water molecules tend to escaped from food surface or sorption sites faster than low storage temperature resulting in least of hysteresis magnitude. However, moisture migration rate also depends on degree of adsorbent porosity and moisture gradient between surrounding air and adsorbent interface (Guillard et al., 2004). Besides that more rigid interaction was demonstrated on surface or interfacial adsorption than bulk adsorption, thus the large hysteresis phenomenon was represented (Matholouthi, 2001). The degree of hysteresis was pronounced in high water activity regions which commonly found in high protein and starchy foods (Swami et al., 2005). The moisture sorption isotherms of all dry food models B-H and B were similar to sorption isotherms of potato starch, prickly pear cladode, dry biscuits and pistachio (Lahsasni, Kouhila, Mahrouz and Fliyou, 2003; McMinn et al., 2005; Yazdani, Sazadehchi, Azizi, and Ghobadi, 2006).

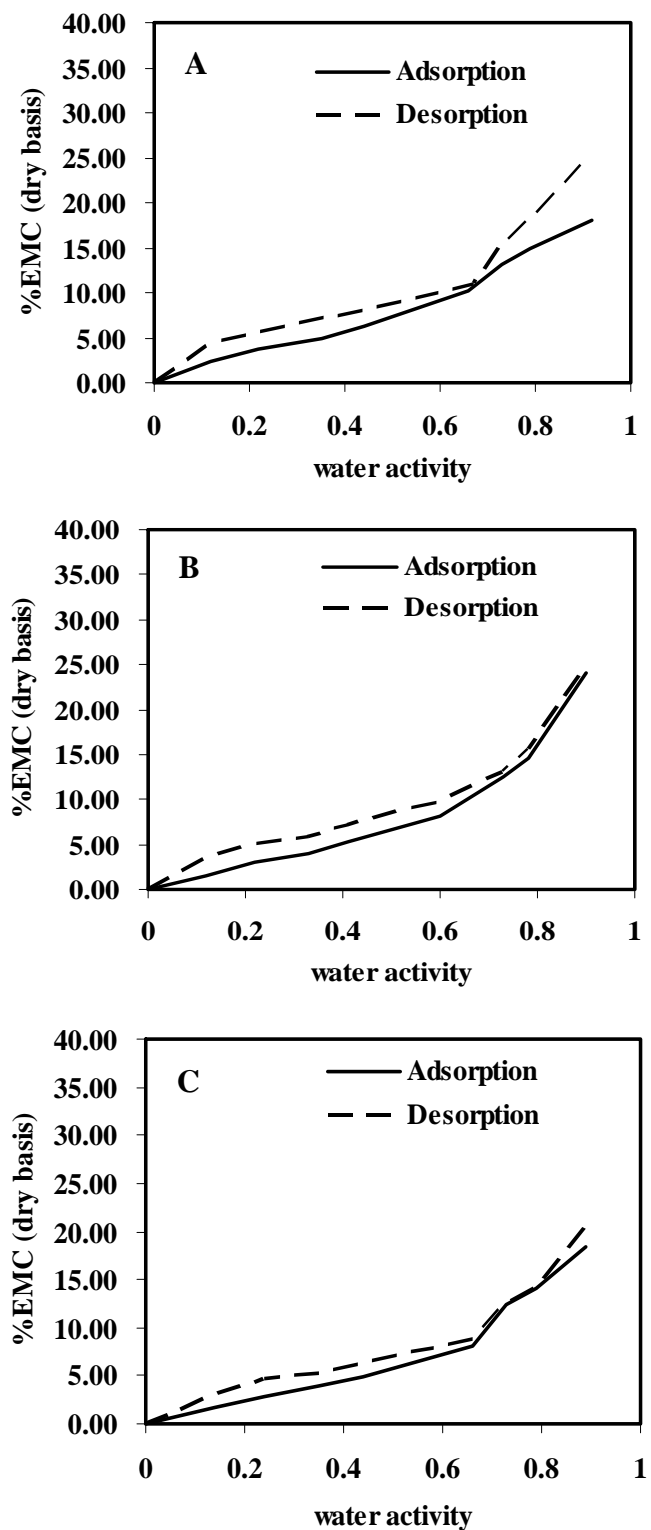


Figure 3.3 Adsorption and desorption isotherms of dry food model B-H at (A) 25, (B) 35 and (C) 45 °C

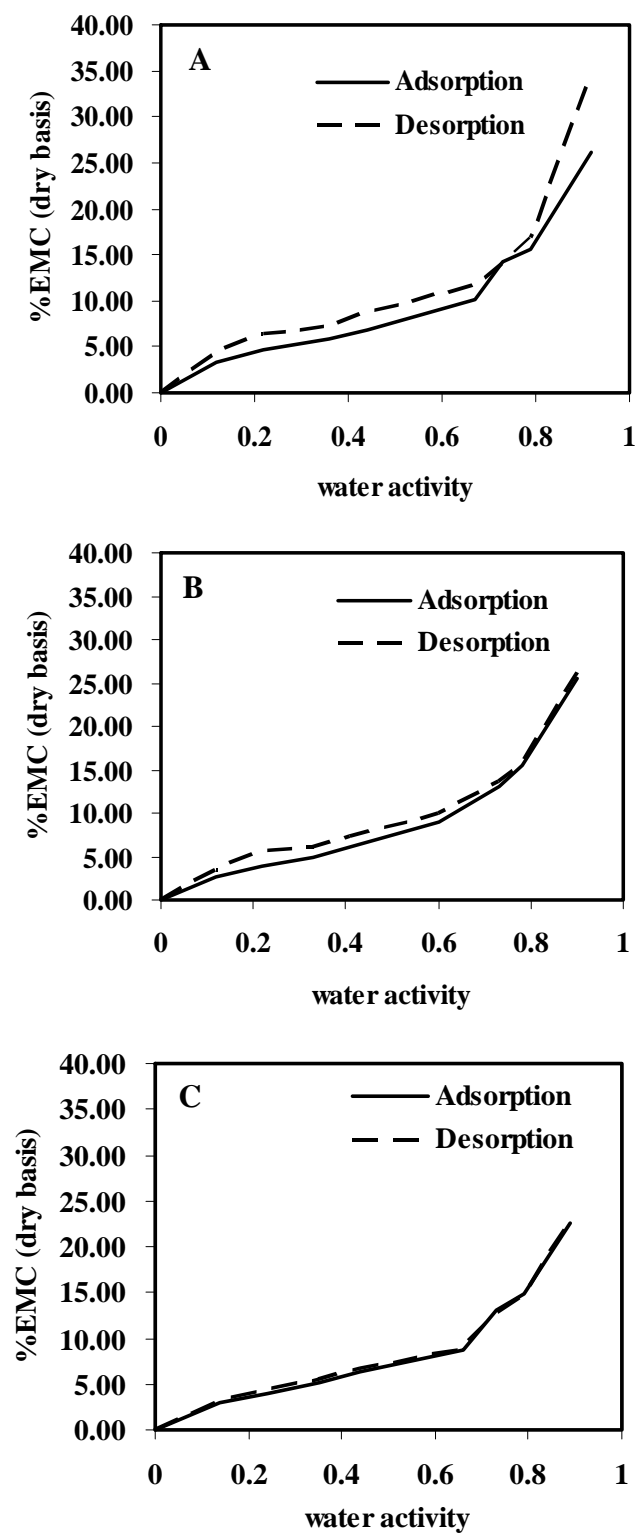


Figure 3.4 Adsorption and desorption isotherms of dry food model B at (A) 25, (B) 35 and (C) 45 °C

3.4.2 Effect of recipes on moisture sorption isotherm

Dry food model studied were classified into two recipes for normal (model A) and model A-H for high protein and fat content. The proximate analyses of dry food models were demonstrated in Table 3.1 which represented closely in their compositions. However, the moisture adsorption isotherm of two recipes exhibited less different between dry food model A and A-H as seen in Fig. 3.5 at storage temperature of 25 °C. The adsorption isotherms of two recipes dry food type B were revealed a difference EMC although similar in their basis components (Fig 3.6). This occurrence might be caused by the different source of protein and fat components containing in the products. Protein and fat types can not identified by crude analysis. Besides that the different of EMC between two recipes affected by forming and expansion ratio of dry food products. Moreover, food structure might not influence on equilibrium moisture content such as the sorption behavior of cereal composite foods but affected by fat content (Roca, Guillard, Guilbert, and Gontard, 2006). At storage temperature of 35 and 45 °C had the same EMC pattern with 25 °C, these phenomenon were found both of model A and B.

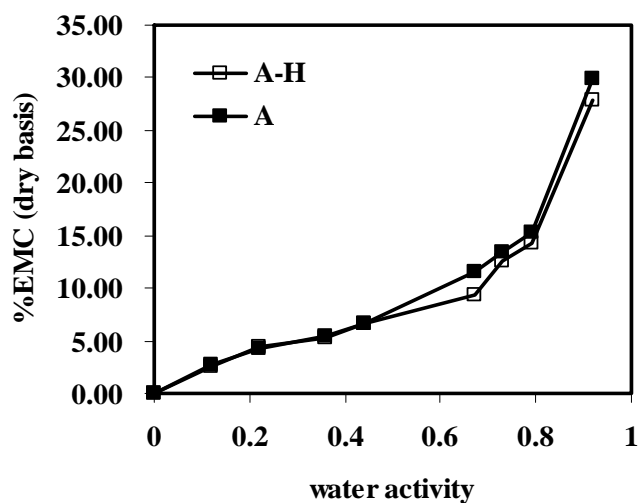


Figure 3.5 Adsorption isotherm of dry food models A-H and A at 25 °C

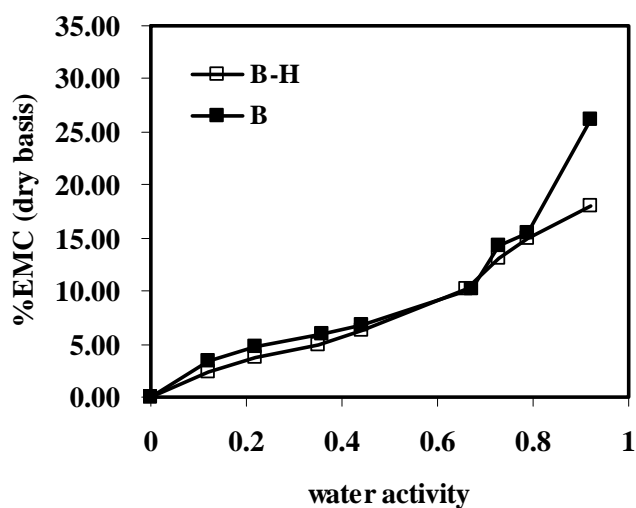


Figure 3.6 Adsorption isotherm of dry food models B-H and B at 25 °C

3.4.3 Effect of temperature on moisture adsorption and desorption isotherms

3.4.3.1 Dry food models A and A-H

The effect of temperature on moisture sorption isotherm was taken into a consideration for dry food model A-H and A as seen in Fig. 3.7 and 3.8, respectively.

Both of desorption and adsorption isotherms were demonstrated a concurrence increase in EMC with decreasing temperature. At constant water activity, higher EMC at the storage temperature of 25 °C than 35 and 45 °C which was clearly display for desorption isotherm. High temperature might be cause of decreasing in surface of sorption sites due to tightly interfacial sorption, thus food products were exhibited more rigid structure than low temperature. The crossing points were found at intermediate to high water activity, these behaviors were accompanied by increasing dissolution effect (Rockland and Beuchat, 1987). The effect of temperatures was similar to various dry food isotherms including cookies and corn snack (Palou, Lopez-Malo, and Argai, 1997).

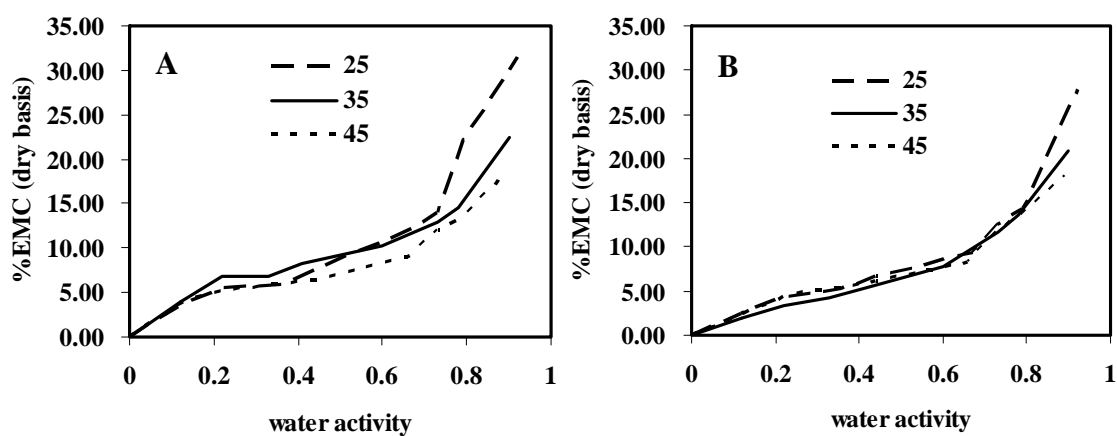


Figure 3.7 Effect of temperature on moisture adsorption (A) and desorption (B) isotherms of dry food model A-H at 25 °C, 35 °C and 45 °C

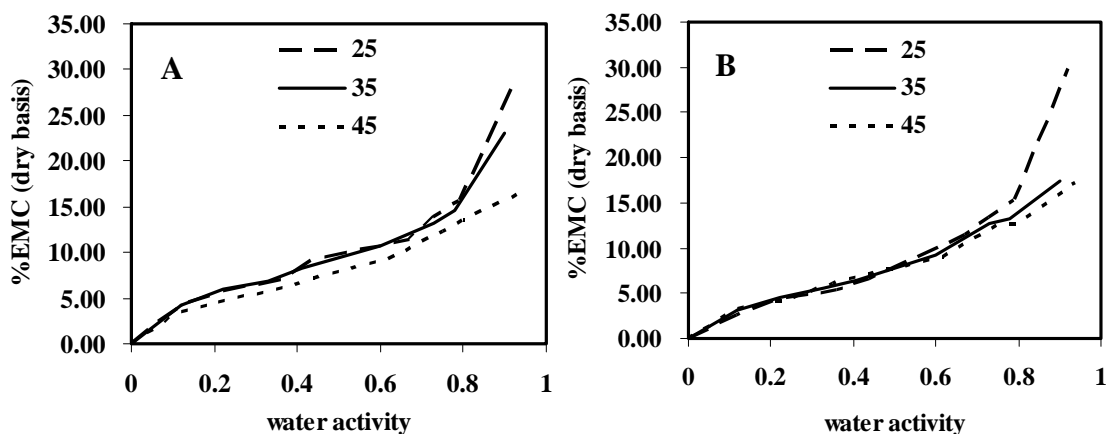


Figure 3.8 Effect of temperature on moisture adsorption (A) and desorption (B) of dry food model A at 25 °C, 35 °C and 45 °C

3.4.3.1 Dry food model B and B-H

The temperature shift was affected on moisture adsorption and desorption isotherms of dry food model B-H and B as seen in Fig. 3.9 and 3.10, respectively. The less temperature effect was pronounced on adsorption than desorption isotherms which found both of dry food model B-H and B. These phenomenon were caused by product swelling during desorption process. At high water activity range, the difference of EMC was obviously shown for adsorption of dry food model B-H but this action was not found for adsorption of dry food model B due to lowering in structural expansion. This behavior was similar with adsorption isotherm of macaroni which stored at 25, 35 and 45 °C (Arslan and Togrul, 2005).

According to the effect of temperature on moisture adsorption and desorption isotherms of all dry food models tested, the increase of temperature caused an increase of water activity for the same moisture content. These actions were increased reaction rate and leading to deterioration. Food products are complex

mixtures of various components, the effect of water content of single food components was important. In company with the relation between water activity and temperature was affected on physical and chemical reactions of food products. However, the effect of temperature was negligible at low to intermediate water activity range which covers the actual moisture content of dry food models studied.

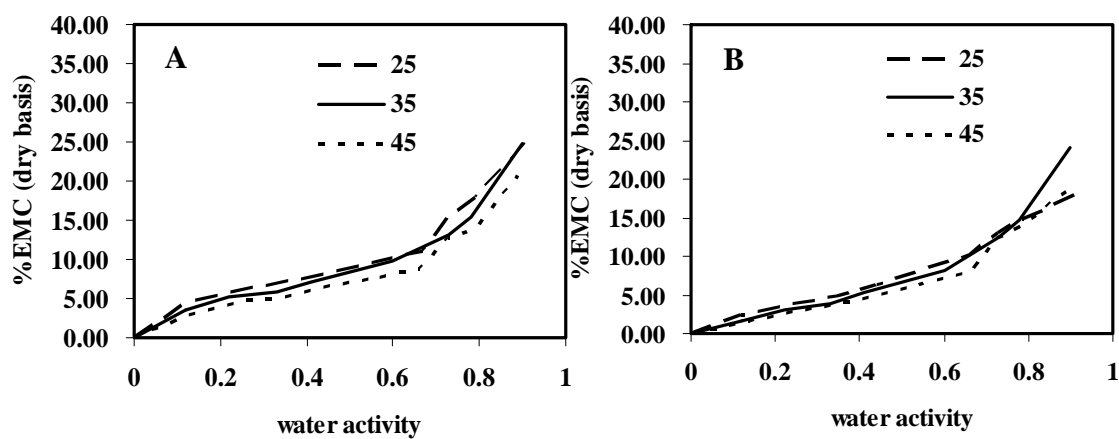


Figure 3.9 Effect of temperature on moisture adsorption (A) and desorption (B) of dry food model B-H at 25 °C, 35 °C and 45 °C

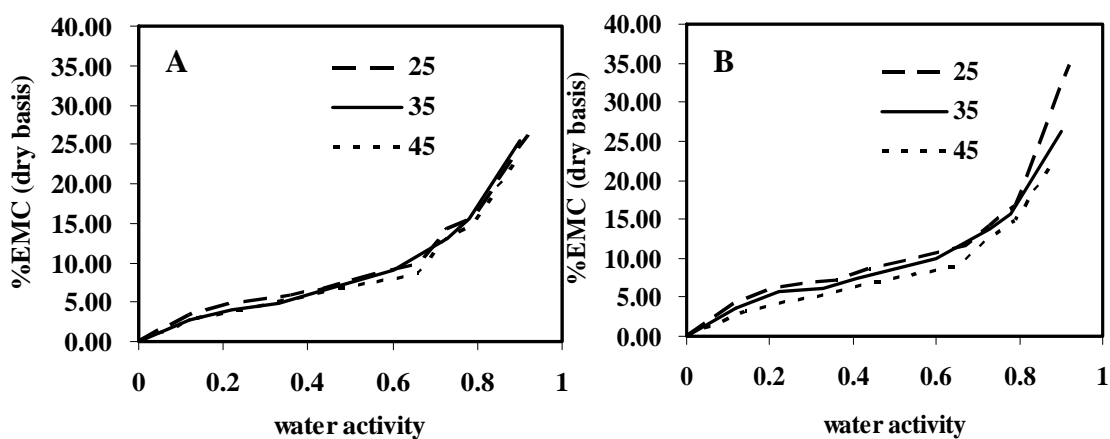


Figure 3.10 Effect of temperature on moisture adsorption (A) and desorption (B) of dry food model B at 25 °C, 35 °C and 45 °C

3.4.4 Mathematical expression for moisture adsorption and desorption isotherms

The experimental sorption equilibrium moisture content data of dry food models were fit to the 5 models; there are BET, GAB, Oswin, Halsey and Chung&Pfoest models. These selecting models were divided by sorption theory for monolayer and multilayer of sorption, only BET model was developed base on monolayer of sorption. The fitting experiments were using non-linear regression analysis. The estimated parameters of sorption model were given as Table 3.4 and 3.5 for dog and cat foods. The GAB model was fit well with the experimental data through the entire ranges of water activity followed by the Halsey models, which pronounced both of dry food model A and B as given in Fig 3.11 and 3.12. The BET model was fit well at low water activity ranges (water activity less than 0.5), while Oswin model gave the poorest fit to the experimental data. Moreover, the best fitting model was confirmed by error estimation parameters, regression coefficient (R^2), mean relative error (MRE), Standard error of estimate (SEE) and residual sum of square (RSS) for type A and type B dry food models were represented in Table 3.6 (A and B) and 3.7 (A and B), respectively. GAB model gave highest R^2 , MRE value less than 10%, and lower SEE and RSS values than Oswin, Halsey and Chung & Pfoest models. The error of sorption model estimations was demonstrated that GAB model was the best suitable model for describing the moisture sorption isotherm of all dry food models. Besides that the acceptability of sorption model was not only related with the ability of fit the experimental data, but the physical and chemical basis was required. GAB model gave the essential information such as monolayer and multilayer of sorption. Sorption model can be used for calculating the moisture

change at different storage conditions. In contrast, the water activities of food products were calculated via sorption isotherm model. The example of model expressions for moisture sorption isotherms were represented as Eq. 3.15-3.19, for moisture adsorption isotherm of dry food model A-H at 25 °C.

$$\text{BET:} \quad M = 0.4277a_w / [(1 - a_w)(1 + (10.2809 - 1)a_w)] \quad (3.15)$$

$$\text{GAB:} \quad M = \frac{0.5899a_w}{[(1 - 0.9356a_w)(1 - 0.9356a_w + 15.5471a_w)]} \quad (3.16)$$

$$\text{Oswin:} \quad M = 0.0708(a_w / 1 - a_w)^{0.5556} \quad (3.17)$$

$$\text{Halsey:} \quad M = \left(\frac{-15.0527}{\ln(a_w)} \right)^{\frac{1}{1.53}} \quad (3.18)$$

$$\text{Chung\&Pfof:} \quad M = 6.1852 + ((-0.0793) \ln(-\ln a_w)) \quad (3.19)$$

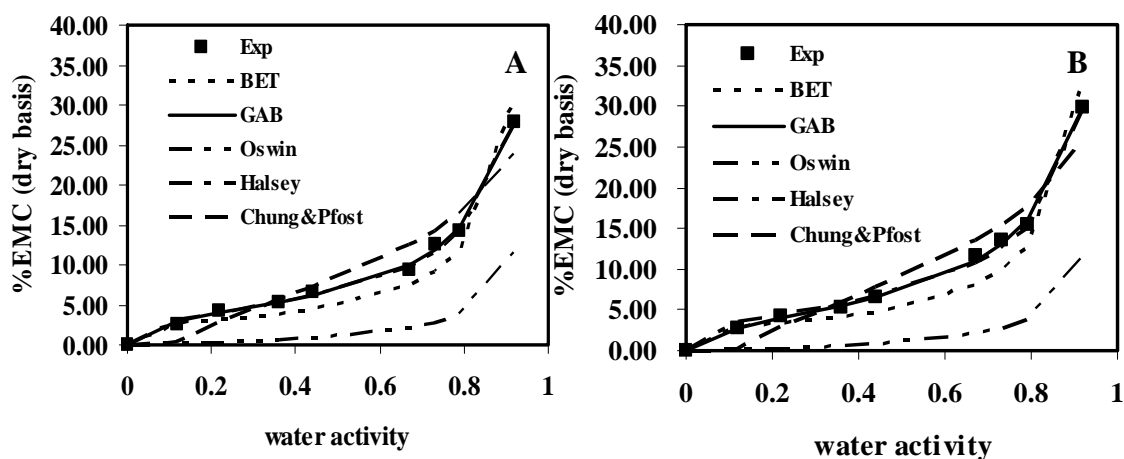


Figure 3.11 Predicted moisture adsorption isotherm of dry foods (A) model A-H and (B) model A at 25 °C using model expressions, experiment, BET, GAB, Oswin, Halsey and Chung&Pfof

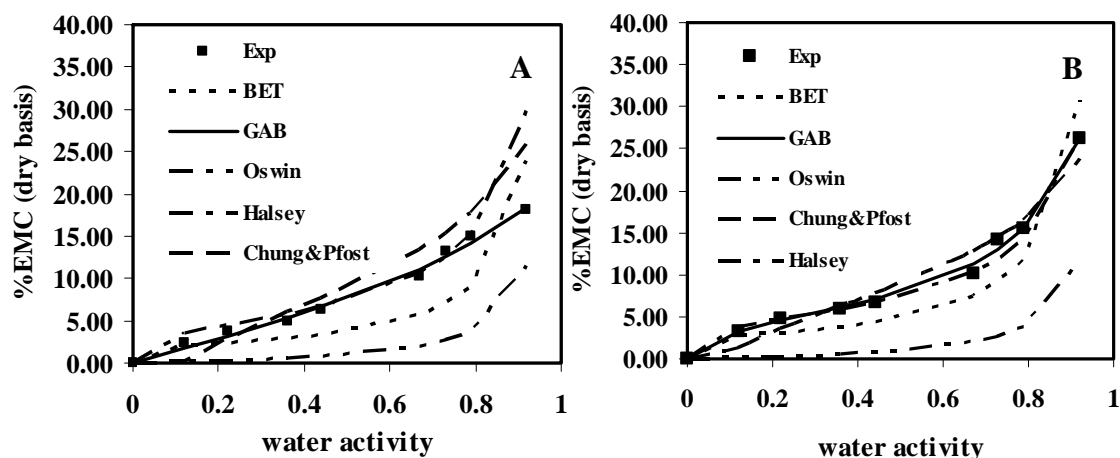


Figure 3.12 Predicted moisture adsorption isotherms of dry food models (A) model B-H and (B) model B at 25 °C using model expressions, experiment, BET, GAB, Oswin, Halsey and Chung&Pfof

Monolayer moisture content (M_0) is significant importance to physical and chemical stability of dehydrated food materials. The M_0 was calculated by BET and GAB models but each sorption models had a different theory development. BET model was investigated base on monolayer, while GAB model applied base on multilayer of sorption (Caurie, 2006; Peng et al., 2007). BET model is only applicable between values of water activity from 0.1 to 0.5 which applied for describe the sorption behavior of foods including dehydrated apple and potato (deMan, 1990). The GAB model can describe covers the entire range of water activity. The M_0 of all dry food models were demonstrated as Fig. 3.13(A)-3.13(D). Monolayer moisture content was calculated by GAB model gave similar with monolayer from BET model. The closely monolayer moisture content might be caused by low initial moisture content, similar composition and production. Monolayer moisture content of food product was varied with their composition and forming. In general the monolayer moisture content

of starchy food was ranging from 3.2-16 %, the monolayer of all dry food models were also demonstrated in this ranges (Palou, et al., 1997). Monolayer moisture content demonstrated temperature independent both of BET and GAB models calculation, this value was increased with increasing temperature. These occurrences were similar to monolayer of cupuassu powder (by spray-dryer) and pestil (Medeiros, et al., 2005; Kaya et al., 2005). Increasing in monolayer was affected by decreasing an interaction between foods components, so many sorption sites were occurred at high storage temperature (Das et al., 2002).

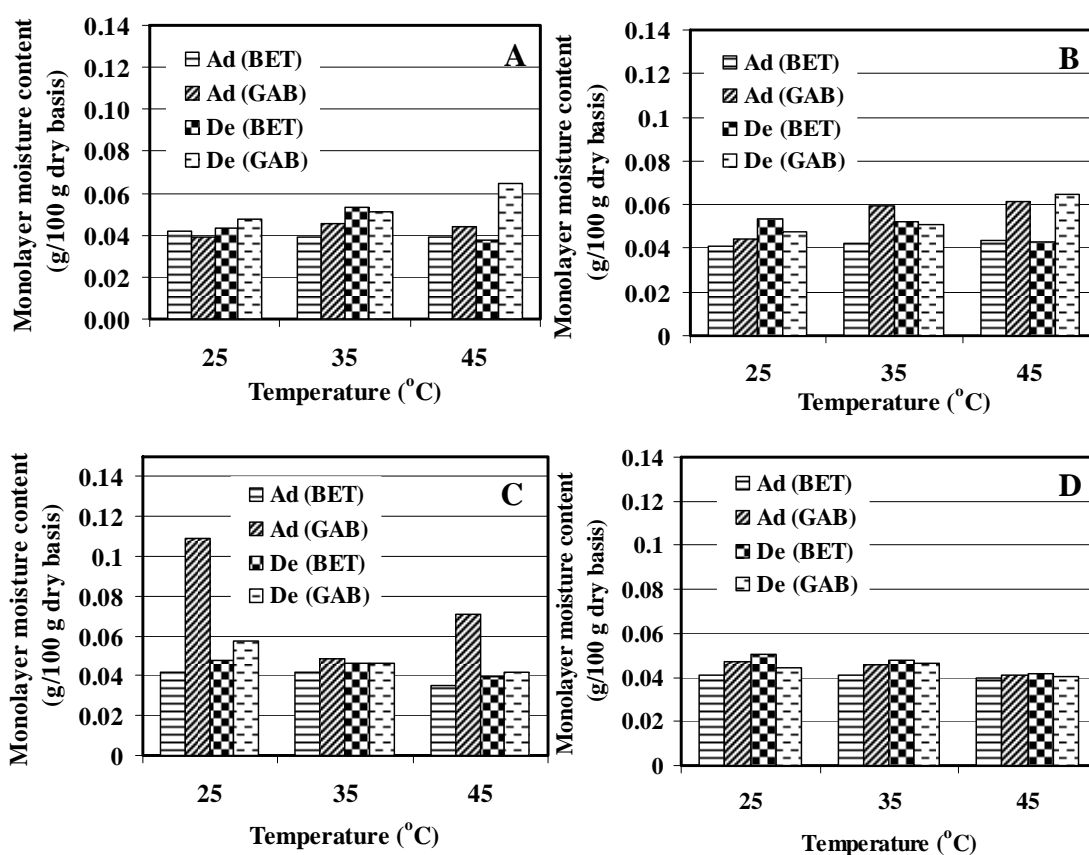


Figure 3.13 Monolayer moisture content (M_0) calculated by BET and GAB model of dry food models (A) model A-H, (B) model A, (C) model B-H, and (D) model B.

Table 3.4 Estimate model constants for adsorption and desorption of dry food model A (H) and A

Dry foods	Models	constant	Adsorption			Desorption		
			25 °C	35 °C	45 °C	25 °C	35 °C	45 °C
Model A-H	BET	M ₀	0.042	0.039	0.039	0.043	0.053	0.038
		C	10.281	6.265	14.491	27.745	20.458	279.664
	GAB	M ₀	0.039	0.046	0.044	0.058	0.051	0.042
		K	0.936	0.880	0.861	0.895	0.858	0.867
		C	16.617	5.200	12.497	7.901	48.765	73.061
	Oswin	N	0.556	0.530	0.455	0.509	0.397	0.410
		K	0.071	0.066	0.071	0.093	0.091	0.077
	Halsey	a	12.754	14.287	16.402	25.172	52.330	17.998
		r	1.513	1.616	1.641	1.657	1.994	1.664
	Chung & Pfof	A	5.833	5.274	5.772	7.378	7.720	6.441
		B	-0.072	-0.062	-0.053	-0.086	-0.056	-0.049
	Model A	BET	M ₀	0.042	0.042	0.044	0.054	0.052
C			11.466	15.284	14.344	16.207	19.766	19.475
GAB		M ₀	0.044	0.059	0.061	0.048	0.051	0.065
		K	0.927	0.756	0.708	0.903	0.863	0.677
		C	10.528	8.146	8.953	65.446	39.170	9.312
Oswin		N	0.554	0.385	0.310	0.454	0.409	0.292
		K	0.077	0.078	0.0780	0.091	0.092	0.080
Halsey		a	15.053	32.726	40.780	35.510	46.064	70.176
		r	1.530	1.929	2.050	1.8135	1.938	2.336
Chung & Pfof		A	6.185	6.372	6.360	7.628	7.696	6.578
		B	-0.079	-0.049	-0.041	-0.069	-0.058	-0.039

Table 3.5 Estimate model constants for adsorption and desorption of dry food
model B-H and B

Dry foods	Models	constant	Adsorption			Desorption		
			25 °C	35 °C	45 °C	25 °C	35 °C	45 °C
Model B-H	BET	M ₀	0.042	0.042	0.035	0.048	0.046	0.040
		C	10.28	3.990	4.638	32.87	16.34	15.36
	GAB	M ₀	0.109	0.049	0.071	0.057	0.047	0.042
		K	0.610	0.900	0.785	0.849	0.904	0.900
		C	2.233	3.418	1.669	17.08	21.08	15.33
	Oswin	N	0.388	0.593	0.551	0.411	0.488	0.497
		K	0.076	0.066	0.062	0.095	0.084	0.072
	Halsey	a	15.016	9.263	10.970	51.246	32.892	17.858
		r	1.529	1.408	1.574	1.985	1.789	1.665
	Chung & Pfof	A	6.185	5.206	4.623	7.763	6.971	5.906
		B	-0.079	-0.073	-0.061	-0.065	-0.067	-0.059
	Model B	BET	M ₀	0.041	0.041	0.040	0.051	0.048
C			21.838	10.166	10.576	35.227	17.697	12.082
GAB		M ₀	0.047	0.046	0.041	0.044	0.047	0.040
		K	0.896	0.917	0.924	0.948	0.915	0.927
		C	14.1340	8.263	10.990	1978.79	27.398	17.569
Oswin		N	0.484	0.555	0.554	0.544	0.495	0.538
		K	0.081	0.076	0.071	0.089	0.086	0.073
Halsey		a	20.726	15.774	13.358	24.971	23.862	14.886
		r	1.689	1.558	1.522	1.609	1.660	1.552
Chung & Pfof		A	6.555	6.162	5.729	7.765	7.237	5.997
		B	-0.069	-0.074	-0.067	-0.084	-0.071	-0.066

Table 3.6(A) Regression coefficient (R^2), Mean relative error (MRE), Standard error of estimate (SEE) and residual sum of square (RSS) for moisture sorption models of dry food models A-H

Sorption models	Dry food model A-H							
	Adsorption				Desorption			
	R^2	MRE	SEE	RSS	R^2	MRE	SEE	RSS
BET(a_w -0-0.4)	0.9900	4.3457	0.2373	0.0481	0.9785	4.2150	0.4261	0.1615
GAB	0.9952	4.4042	0.4199	0.1799	0.9881	5.4115	0.8279	0.7965
Oswin	0.9931	5.6934	0.5407	0.2706	0.9847	4.9263	0.9366	0.9856
Halsey	0.9873	9.4012	0.7720	0.5320	0.9817	4.6476	0.7948	0.5877
Chung& Pfof	0.9793	16.3907	1.3981	2.0432	0.9589	11.1994	1.5282	2.4466

Table 3.6(B) Regression coefficient (R^2), Mean relative error (MRE), Standard error of estimate (SEE) and residual sum of square (RSS) for moisture sorption models of dry food models A

Sorption models	Dry food model A							
	Adsorption				Desorption			
	R^2	MRE	SEE	RSS	R^2	MRE	SEE	RSS
BET(a_w -0-0.4)	0.9965	2.3960	0.1515	0.0198	0.9958	1.8614	0.1825	0.0367
GAB	0.9968	3.2540	0.3410	0.1048	0.9946	4.3948	0.5022	0.2434
Oswin	0.9866	6.0167	0.6056	0.3751	0.9846	5.7359	0.7280	0.5131
Halsey	0.9576	10.4386	0.9550	0.8801	0.9723	6.6671	0.7214	0.5435
Chung& Pfof	0.9762	10.5910	1.0234	1.5171	0.9681	8.7672	1.2125	1.5661

Table 3.7 (A) Regression coefficient (R^2), Mean relative error (MRE), Standard error of estimate (SEE) and residual sum of square

(RSS) for moisture sorption models of dry food models B-H

Sorption models	Dry food model B-H							
	Adsorption				Desorption			
	R^2	MRE	SEE	RSS	R^2	MRE	SEE	RSS
BET(a_w 0-0.4)	0.9975	4.3308	0.1966	0.0459	0.9952	2.6625	0.1871	0.0283
GAB	0.9937	5.8515	0.4572	0.2948	0.9942	3.5058	0.4971	0.2741
Oswin	0.9754	11.9775	0.9214	0.8967	0.9916	4.5623	0.6282	0.4059
Halsey	0.9819	14.0917	0.8670	0.6909	0.9882	6.4150	0.7551	0.5181
Chung& Pfof	0.9610	21.8016	1.5353	2.3335	0.9654	12.5354	0.8946	1.5927

Table 3.7 (B) Regression coefficient (R^2), Mean relative error (MRE), Standard error of estimate (SEE) and residual sum of square (RSS) for moisture sorption models of dry food models B

Sorption models	Dry food model B							
	Adsorption				Desorption			
	R^2	MRE	SEE	RSS	R^2	MRE	SEE	RSS
BET(a_w 0-0.4)	0.9980	1.3320	0.1842	0.0102	0.9925	3.1337	0.4951	0.0557
GAB	0.9963	2.6877	0.1467	0.1860	0.9967	4.5702	0.1678	0.2170
Oswin	0.9952	4.3279	0.1721	0.2426	0.9908	8.0347	0.2903	0.7169
Halsey	0.9921	6.6638	0.2623	0.4898	0.9960	4.5403	0.2197	0.3588
Chung& Pfof	0.9565	16.819	0.5629	2.2545	0.9317	17.624	0.7722	4.7808

3.4.5 Thermodynamic properties of dry food models

3.4.5.1 Isostatic heat of sorption

The isosteric heat of sorption or differential enthalpy directly relates to moisture sorption characteristic of food product. Isostatic heat of adsorption and desorption represents the heat releasing and heat requirement that involved with adsorption and desorption processes, respectively. Isostatic heat of adsorption and desorption for dry food models were evaluated by using Eq. 3.14. The isosteric heat of adsorption and desorption for dry food models A-H and A were demonstrated as Fig 3.14 and 3.15, respectively. The highest heat releasing of adsorption isotherm was found at the low moisture content. These patterns of heat releasing were represented both of dry food model A-H and A. Higher isosteric heat of sorption was observed for desorption process rather than the adsorption process throughout the entire range of water activity. Because a moisture pre-doped procedure at the sample preparation step of desorption experiment was created an irreversible changes of their structure. Therefore, desorption samples must be required more energy to evaporate extra amount of moisture before reaching a saturation. As a result of high energy input, water molecules at outer layer tend to escape away from adsorbent (Yazdini, et al., 2006). Nevertheless, many water molecules were still remained inside the capillary or pore sites of food thus desorption process ends with a relatively high moisture content at any given equilibrium condition.

A comparison of the isosteric heat of sorption between dry food models A-H and A demonstrated that the energy was at a higher level for dry food model A due to a different of their composition and forming in each product. However, fewer changes

of isosteric heat of sorption were exhibited at high moisture content both of adsorption and desorption, but this change was obviously found in dry food model A.

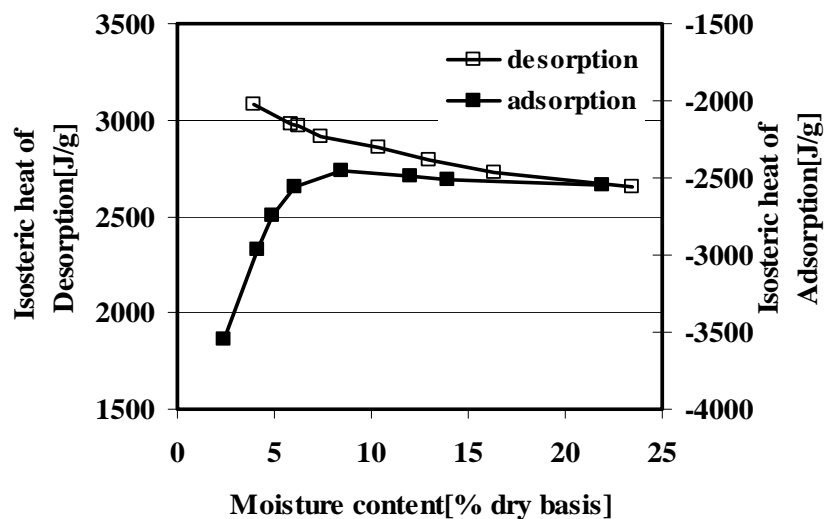


Figure 3.14 Isosteric heat of adsorption and desorption for dry food model A-H

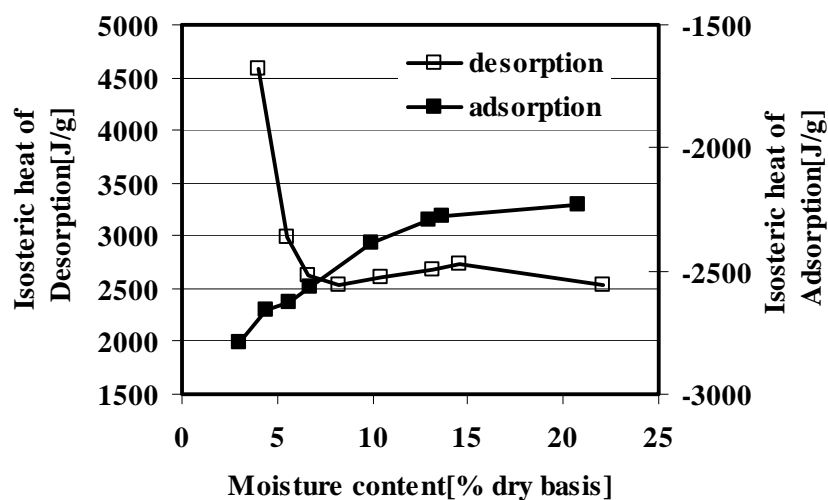


Figure 3.15 Isosteric heat of adsorption and desorption for dry food model A

The isosteric heat of adsorption and desorption for dry food models B-H and B were determined as the isosteric heat of sorption of dry food models A as described previously. The isosteric heat of desorption was higher than the isosteric heat of

adsorption as shown in Fig 3.16 and 3.17 for dry food model B-H and B, respectively. Isothermic heat of adsorption showed no significant difference between dry food model B-H and B, excluding the isothermic heat of desorption was represented the higher energy level of dry food model B than B-H.

According to result of isothermic heat of sorption, the difference energy level of all dry food models due to different of initial moisture content and kibble size and shape. The difference of isothermic heat between adsorption and desorption were obviously found at low moisture content, because these appearances were greatly affected by the interaction between moisture and food surface during the sample preparation (moisture preparation step). On the other hand, the lower available sorption sites were occurred at high moisture content and resulting in low isothermic heat of sorption (Tunc et al., 2007). Besides that the multilayer of sorption was generated at high moisture content with respect to a low isothermic heat of sorption since the energy level involved with water-water interaction was less than the one for water-food surface interaction. Comparing to the heat of condensation of pure water was lower than the heat of water vaporization from food matrix. Therefore at high moisture content, isothermic heat of adsorption and desorption were closely with latent heat of vaporization of pure water (Mulet, Garcia-Roverter, Sanjuan, and Bon, 1999; Resio, Aguerre, and Suarez, 1999).

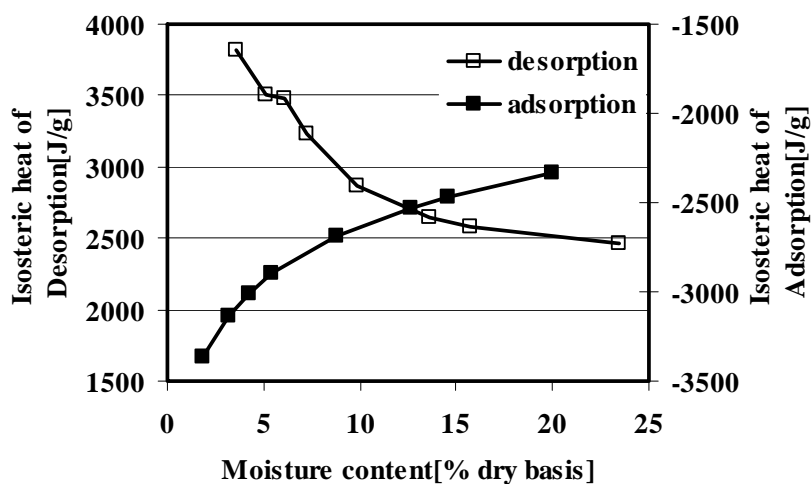


Figure 3.16 Isosteric heat of adsorption and desorption for dry food model B-H

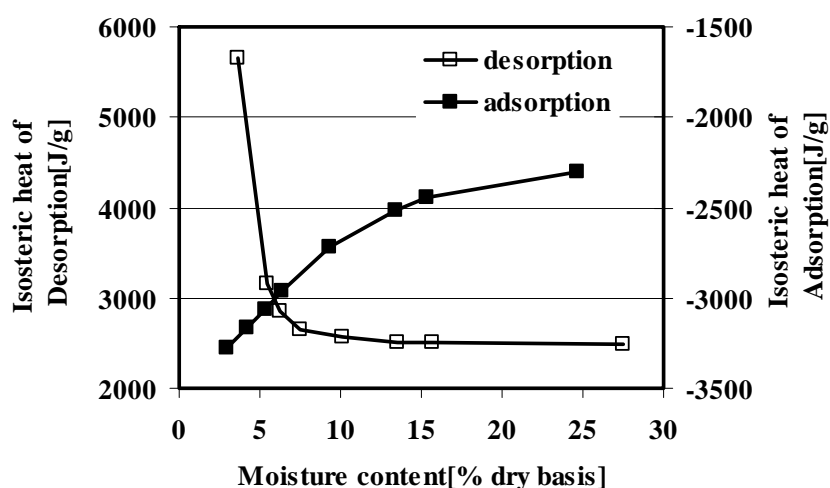


Figure 3.17 Isosteric heat of adsorption and desorption for dry food model B

3.4.5.2 Entropy of sorption

The entropy of sorption for dry food model was calculated via Eq. 3.14. The entropy of sorption related to a number of available sorption sites existing in sorption system (McMinn et al., 2005). The entropy of adsorption and desorption of dry food model A-H were showed in Fig. 3.18, and these values exhibited a decreasing function of moisture content. Entropy of adsorption was slightly lower

than the entropy of desorption through an entire range of moisture content because the moisture adding step of desorption experiment created more structural opening and sorption sites. The negative entropy of adsorption indicate the lower hydration level with increasing moisture content, this phenomena was similar to the entropy of sorption of carbohydrate polymer and macadamia nut (Perez-Alonso et al., 2006; Dominguez et al., 2007).

The entropy of sorption for dry food model A was showed as in Fig. 3.19 and entropy of sorption was also a decreasing function of moisture content liked the results of dry food model A-H. The similar entropy of adsorption and desorption were found through the whole range of moisture content. Furthermore, the effects of an interaction between water-food surface and water-water interaction at the sorption sites were a major reason of decreasing in available of sorption sites, specifically at high moisture content. In opposite to these results, at high moisture content, the entropy of adsorption was found to increase at higher amount of moisture content due to swelling of products which high protein containing (Viollaz, and Rovedo, 1999).

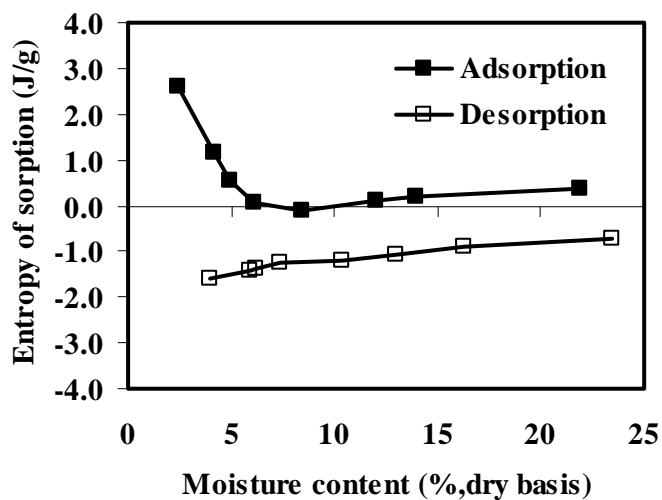


Figure 3.18 Entropy of adsorption and desorption for dry food model A-H

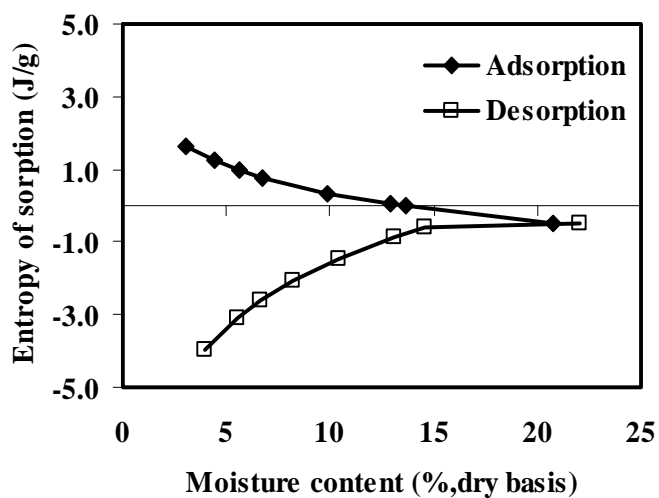


Figure 3.19 Entropy of adsorption and desorption for dry food model A

The entropy of adsorption and desorption for dry food model B-H and B were showed in Fig. 3.20 and 3.21, respectively. The entropy of sorption was also decreasing function of moisture content. All the entropy of desorption were higher than entropy of adsorption because water molecules had more moving ability during desorption than the adsorption as found for the case of starch powder (Al-Muhtaseb et

al., 2004). Low entropy of sorption may occur by the effect of fat or lipid content which its hydrophobic group was unable to interact with hydrophilic molecules.

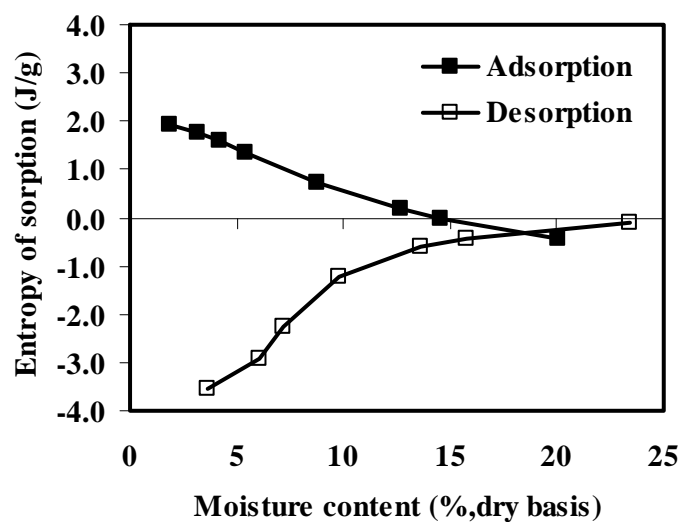


Figure 3.20 Entropy of adsorption and desorption for dry food model B-H

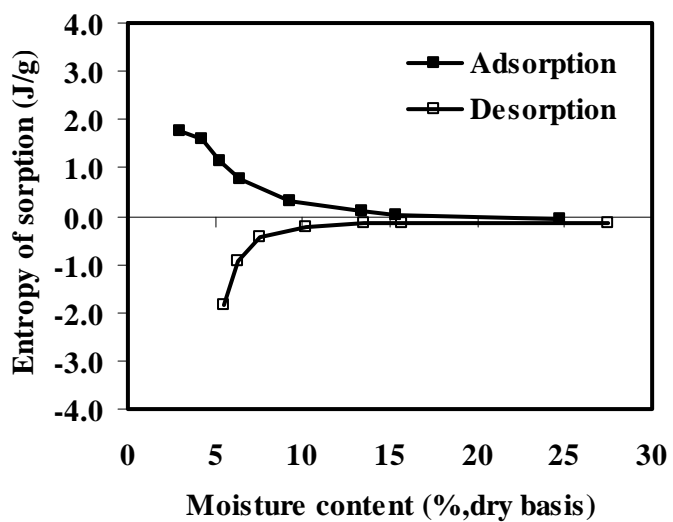


Figure 3.21 Entropy of adsorption and desorption for dry food model B

3.5 Conclusions

Moisture adsorption and desorption isotherms of all dry food models studied were represented as type II isotherm (S-shape). The effect of recipes on moisture adsorption and desorption isotherms were found of dry food models studied. The effect of temperature on moisture sorption isotherm was identified. Moisture content was decreased with increasing temperature while the correspondent water activities trend to increase with storage temperature. GAB was the best suitable model for describing the moisture sorption isotherm of all dry food models studied. Monolayer moisture content of dry food models studied was temperature independence. Both isosteric heat of adsorption and desorption were a decreasing function with moisture content. The isosteric of adsorption was lower than desorption which determined throughout the whole range of water. The entropy of sorption was represented a decreasing function of moisture content, the highest entropy of sorption was found at low moisture content.

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CHAPTER IV

LIPID OXIDATION AND OFF-ODOR EVALUATION OF DRY FOODS MODELS

4.1 Abstract

The studies of lipid oxidation and odor changing characteristic were conducted for dry food models. Two dry food models were subjected for model A and B which made with different protein sources. Each model consisted of dry food with regular protein and another with high protein. All dry food models were different in their physical properties. The extent of lipid oxidation was accounted for the effect of storage temperature and concentration of BHA/BHT in the products. Lipid oxidation was evaluated for the effect of storage temperature at 35, 45 and 55 °C for 3 months. Dry foods with high level BHA/BHT (commercial formula) in both models had lower TBARS and hexanal contents than the inevitable adding formula (IAF or a minute concentration of BHA/BHT) for all storage temperatures. TBARS and hexanal contents of all samples increased with storage time and temperature. Off-odor of CUF and IAF was stronger at a longer storage time and high temperature but no significant differences of off-odor were found in both food models. The kinetic rate of lipid oxidation reaction was obtained for the IAF samples with the activation energy of TBARS and hexanal were at 28.69 and 65.64 kJ/mol. Long term storage was conducted for the commercial dry foods with high BHA/BHT at 32 °C for 18 months, the TBARS and hexanal contents were found to be constantly low throughout storage time. It

was suggested that the rejection level of TBARS and hexanal for these dry food products were 4.8 $\mu\text{g/g}$ and 1.67 ng/g , respectively.

Keywords: Lipid oxidation, dry food products, off-odor evaluation, kinetic rate of reaction

4.2 Introduction

Dry foods are classified as ready to eat foods which more nutritious, convenience for use, less cooking time. Almost of dry foods are produced by extrusion process which make product porosity and may enhance susceptibility to many reactions (Sun, Senecal, Chinachoti, and Faustman, 2001). The main ingredients of dry foods are carbohydrates and proteins from many sources of raw materials including cereal, soybean, meat and chicken by products and others.

Many food additives are added in dry food production such as sugar, salt, sauce and other preservative substances to improve the taste of products and to prevent the spoilage microorganism for longer shelf-life. In general, dry foods have long shelf life stability because they contain low moisture content. However, the physicochemical changes of dry product are the most important problem which may occur during storage, transportation and after distribution to consumer. The moisture content of dry food ingredients are required for controlling because they may affect any changes in food products. The moisture contents of dry food products were used as a tool for selecting the appropriate packaging materials in order to control a properly moisture content and residual nutritious throughout storage time. However, the extrusion process can take effects on dry food product including nutritional values, product stability and textural changes (Lasekan, Idowu and Ojo, 1996). Thus dry food industries have to control and prevent the significant chemical reactions which respect to product off-odor and nutrition losing during production and distribution. The off-

odor evolution of food can be prevented by storing at appropriate conditions such as modified atmosphere packaging and safety distribution such as avoiding contraction between foods and packaging or tightly sealed from contaminant compounds (Pettersen, Eie, and Nilsson, 2005; Kim et al., 2006).

Lipid oxidation is an important chemical reaction which causes rancidity or off-odor, color changing and toxic compounds formation of food products (Muik, Lendl, Molina-Diaz, and Ayora-Canada, 2005; Shaker, 2006). Decreasing in consumer acceptance and shelf-life stability are depending on degree of lipid oxidation. Dry foods are low moisture foods due to high pressure and temperature production thus some deterioration reactions can not easily occur including microbial growth. High temperature and pressure are used for extrusion process which can destroy pathogenic and spoilage microorganism but might affect the chemical reactions between amino acids and reducing sugars (Maillard reactions) resulting in product browning (Ames, 1996). Moreover, some deterioration rates are occurred at relative low water activity including lipid oxidation, enzymatic and non-enzymatic reactions (Sun et al., 2001). Low moisture food is preferred for lipid oxidation due to directly interaction between food surface and oxygen or reactive compounds. The unsaturated fatty acid is the most important compound for lipid oxidation due to double bond containing as a result oxygen or reactive compound can react together. The concentrations of lipid oxidation products both of primary and secondary oxidation products depend on degree of unsaturated fatty acids. Secondary lipid oxidation products are normally evaluated via unstable primary product such as hydroperoxides which take many effects on consumer acceptance (Pettersen, Eie and Nilsson, 2005). In addition, lipid oxidation rate depends on various factors including oxygen concentration, amount of reactive compounds, light exposure and storage temperature. The secondary lipid

oxidation products including aldehydes, ketones and alcohols are taking an effect on rancidity or product off-odor.

Antioxidants are natural or synthetic compounds which can delay or inhibit lipid oxidation reaction. BHA (Butylated hydroxyanisole) and BHT (Butylated hydroxytoluene) are synthetic antioxidants and normally used for inhibiting lipid oxidation in most food products especially high fat containing foods. These antioxidants represent high efficiency by reacting with catalyst of lipid oxidation or act as hydrogen donor (Jahan, Paterson, and Spickett, 2004). Duan and others (1998) reported that BHA and BHT gave the highest antioxidant efficiency in ferric chloride solution than others synthetic antioxidants. The lower of color and TBARS changes in meat product with added BHA than no added BHA, indicated high antioxidant activity of synthetic antioxidant (Aksu and Kaya, 2005).

According to the problem of lipid oxidation of dry food products, this research aimed to study the effect of antioxidant on lipid oxidation of two dry food models. Lipid oxidation products were compared between normal dry products and dry product with high protein/fat content. TBARS and hexanal contents of the products were determined. Sensory evaluation was performed for off-odor attribute using Quantitative Descriptive Analysis (QDA) method. All dry food samples were stored at 35, 45 and 55 °C for 3 months prior to analyses. A long term investigation was also conducted to monitor the actual shelf life stability of the dry food products as normally practice in industries by storing the food samples at 32 °C for 18 months.

4.3 Material and methods

4.3.1 Materials

Two types of commercial dry foods made from different protein sources were obtained from local factory and assigned as dry food model A and B. Within each model, there were two dry food products made with normal (Model A and Model B) and high protein/fat contents (Model A-H and Model B-H) all of which high amounts of antioxidant (BHA/BHT) was added for oxidation protection (Table 4.1).

For investigation of the effect of antioxidant on dry food oxidation, dry food products of Model A and Model B with high BHA/BHT (a commercial use formula, CUF) and with minute amounts (0.0064%) of BHA/BHT (an inevitable adding formula, IAF) were also obtained from the same factory.

All dry food samples were separately packed in tightly sealed packages, kept at 4-10 °C during shipment and stored at -20 °C until use.

Table 4.1 Proximate compositions of all testing samples

Dry food	Composition (% in finished good)			
	Protein	Lipid	Fiber	Moisture
Model A-H	26.00	12.00	5.00	7.50
Model A	18.00	10.00	5.00	7.50
Model B-H	30.00	12.00	4.50	7.50
Model B	26.00	10.00	5.00	7.50

*H= High protein /fat content

4.3.2 Chemicals

Triobarbituric acid (TBA) and Butylatehydroxyanisole (BHA) were purchased from Fluka Chemie GmbH (Buchs,Germany). Thichloroacetic acid (TCA) was purchased from Carlo Erba Reagenti (Strada Rivoltana, Rodano, MI(I)). 1,1,3,3-

tetraethoxypropane (TEP) and hexanal were purchased from Sigma-Aldrich Chemie GmbH (Steinheim Germany).

4.3.3 Sample preparation

Samples were weighted (30 g) and repacked into a (15 x 23 cm) vacuum bag and tightly sealed. Duplicate sample bags were made for each analysis of TBARS and hexanal. For hexanal determination, the sample bag was stricken with silicone septum in order to be used as a gas sampling port. Hexanal content was determined in one bag throughout experimental time. All samples were kept into control chambers setting at 35, 45 and 55 °C \pm 1, for the whole course of testing time.

4.3.4 Sample storage method

For acceleration test, all samples were kept in temperature control chambers setting at 35, 45 and 55 °C for 3 months. The samples of Model A-H and A, and Model B-H and B were taken for chemical and sensory analyses once a week. For the effect of antioxidant, the CUF and IAF samples were taken at 3 day interval for the first month and 12 day interval for the last two months.

For long term study, the dry food samples of Model A-H, A, B-H and B were packed in non-gas type barrier plastic bags and stored at 32 °C for 18 months. The samples were taken every month for chemical and sensory analyses.

4.3.5 Chemical analysis

4.3.5.1 TBARS (Thiobarbituric acid reactive substances) analysis

Sample (5 g) was mixed with 50 ml of de-ionized water, then adjusted pH to 1.5 with 4.0 M HCl. BHA of 500 μ l (1.5% in ethanol) and few drops of antifoam were added. The sample solution was distilled by direct distillation, and 25 ml distillate was collected.

Standard 1,1,3,3-tetraethoxypropane (TEP) was used. TEP (100 mg) was hydrolyzed to MDA with 0.1 N HCl (10 ml) by heating in boiling water for 5 min, and cooled to room temperature in tap water. The hydrolyzed TEP was used as MDA standard solution. The MDA standard solutions in the range of 0.25 – 4.00 µg/ml were used for constructing a calibration curve.

Five ml of sample distillate or MDA standard solution was mixed with 5 ml of 0.02 M TBA, incubated in 90 °C water bath for 30 min, cooled to room temperature in tap water, and measured absorbance at 532 nm. TBARS value was calculated from the calibration curve of the MDA standard.

4.3.5.2 Hexanal analysis

Hexanal content was measured by gas chromatography (GC) equipped with flame ionization detector (FID) (Varian CP3800, Thai Unique, Co, Ltd). Volatile compounds were separated by a VF-1MS capillary column (30 m length, 250 µm internal diameter, 0.35 µm film thickness containing 100% dimethylpolydioxane as a stationary phase). Helium was used as a carrier gas with flow rate at 2.0 ml/min. Split mode was set at a split ratio of 1 to 10 after 0.5 min injection. The temperature program of the GC oven was set as follows: an initial temperature of 40 °C was set for 5 min, then the temperature was increased at a rate of 10 °C /min to 150 °C after that the rate was changed to 40 °C /min until reaching 200 °C and hold for 2 min. Injector temperature was set at 220 °C, and detector was maintained at 280 °C and. All samples were drawn by 1.0 ml gas tight syringe (EXMSGAN 100, ITO Corporation, Fuji, Japan) then injected onto the GC. The standard hexanal was prepared into acetonitrile at the concentration 0.5 -10.0 ppm, then 0.5 µl was injected onto GC for hexanal calibration curve.

4.3.6 Off- odor evaluation

Samples were repacked into small vacuum bags, tightly sealed and stored in temperature control chambers which were set at 35, 45 and 55 °C. Twelve experience panelists were recruited for hexanal perception using ranking method. The hexanal solutions at concentrations of 0.15, 0.5, 2.5, 15 and 150 ppm solutions were used for 3 sessions of perception practices. Eight panelists were selected for off-odor training using actual dry food products using the CUF and IAF samples which were stored at 55 °C for 1-7 weeks and kept at -20 °C prior to evaluation. The off-odor evaluation was achieved using quantitative descriptive analysis (QDA) method. All samples were reconditioned at 25 °C for at least 1 hr before evaluation. Panelists were instructed to open the sealed samples and assess off-odor by comparing with control sample.

The off-odor intensity was indicated by placing a vertical line across the 10-cm unstructured scale and the quantity of difference were reported in centimeter (Gomes, Silva, Cardello, and Cipolli, 2003; Piagentini, Mendez, Guemes, and Pirovani, 2005). The intensity scales were converted into six category scales, barely detectable, weak, moderate, strong, very strong and strongest (Lawless and Heymann, 1998). The statistical analysis was using Statistical Analysis System (SAS, 1997) with a significance level of $P = 0.05$.

4.3.7 Kinetic rate analysis

The chemical data, the changing amount of TBARS and hexanal with time were applied for determining a kinetic rate of lipid oxidation for each dry food model. Since the lipid oxidation is 1st order reaction, changing amount of lipid oxidation products with respect to time must follow the form of equation 4.1 (Vazquez-Landaverde, Qian, and Torres, 2007).

$$\frac{dC}{dt} = kC \quad (4.1)$$

where: C is a product concentration at any time, k is a reaction rate constant, and t is a storage time. The solution for Eq (4-1) was in the form of Eq. (4.2) and (4.3).

$$\ln(C) = k(t - t_0) + \ln C_0 \quad (4.2)$$

or

$$C = e^{k(t-t_0)} + C_0 \quad (4.3)$$

where: C₀ is a concentration at initial time (t₀) of a lipid oxidation product.

The effect of temperature on the reaction rate constant (k) was assumed to follow the Arrhenius relation as shown in Eq. (4.4) (Jin, Kishita, Moriya, and Enomoto, 2001; Tarade, Singhal, Jayram, and Pindit, 2006).

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right) \quad (4.4)$$

where: E_a is activation energy of reaction (kJ/mol), R is a universal gas constant (8.314 J/mol K), and T is temperature (K).

4.4 Results and discussion

4.4.1 Effect of antioxidant on lipid oxidation of dry food model

The efficacy of antioxidants (BHA and BHT) on inhibition of lipid oxidation was reported in this section. The product deterioration was measured in terms of TBARS and hexanal contents in the stored samples. Both compounds were the secondary products of lipid oxidation. To facilitate readers, two groups of samples mentioned here were repeatedly defined as a commercial use formula (CUF) made with high

concentration of BHA/BHT and an inevitable adding formula (IAF) made with minute amounts of BHA/BHT.

The TBARS contents of the CUF samples were lower than those of IAF samples for all testing temperature as expressed in Fig. 4.1. However, the difference of TBARS contents between the sample groups stored at 35 °C was noticeable while an obvious different of TBARS content was observed for the remaining high storage temperatures. A plateau profile of TBARS contents found in both cases after a certain storage time revealed that there was an effect of antioxidant activity on the IAF samples. It was also suggested that the IAF sample had enough antioxidants to slow down or retard the onset of lipid oxidation. In addition, low TBARS of IAF sample could be due to some natural antioxidant present in the samples.

In general, TBARS method is lack of specificity due to reacting of TBA with other compounds but the spectrophotometer was set to measure at 532 nm that an absorbance wavelength specific for MDA (malondialdehyde) or pink color solution. Yet, TBARS method is widely applied to identify the lipid oxidation for many food systems i.e. freeze dried beef product, irradiated pork loin and pistachio nut paste (Sun et al., 2001; Zhu, Mendonca and Ahn, 2004; Gamli and Hayoglu, 2007). Therefore, an assessment of the lipid oxidation in this work was also done by tracking a hexanal content which is a major compound definitely found in rancidity products. Since the hexanal in gas phase is analyzed by GC, on the other hand, hexanal measurement is much more sensitive and reliable than any other analytical methods used for identification of lipid oxidation products.

The changing amounts of hexanal with storage time for each sample are shown in Fig. 4.2. According to TBARS and hexanal profiles at 35, 45 and 55 °C, increasing heat content by storage at high temperatures could accelerate lipid oxidation and

reduce the activity of BHA/BHT. However, BHA/BHT is proved to inhibit the lipid oxidation by acting as hydrogen donors or free-radical acceptors (Saxby, 1996; Bautista-Teruel et al., 1999).

All CUF samples at every storage temperatures had lower hexanal contents than did IAF samples. However, from hexanal analysis it was found that inhibitory activity of antioxidant used started to be inefficient when the storage temperature was beyond 45 °C. High antioxidant efficiency was found due to the plateau of hexanal content for the IAF sample at 35 °C throughout storage time. Although the CUF sample gave lower hexanal content than IAF sample (Fig. 4.2 (A)), but the result demonstrated that the inevitable adding of BHA/BHT could reduce the lipid oxidation reaction at 35 °C. The hexanal contents at 45 and 55 °C of IAF samples obviously increased and higher ($p < 0.05$) than CUF sample, thus high concentration of antioxidant in product formula could efficiently retard the lipid oxidation of dry food model A at high storage temperature. Furthermore, the amounts of lipid oxidation depend on many factors such as degree of unsaturated fats, oxygen concentration, surface area and water content. In addition, the extrusion process is set to make an expanded product causing an increasing of surface area and might be increase the fat surface exposed to oxygen or air which catalyzed the lipid oxidation. Moreover, the catalysts of lipid oxidation may be from the wearing of screw and barrel during extrusion process (Camire et al., 2005). All dry food models studied were stored in plastic bag, thus changing in their water activity should be very minimal and not effect on lipid oxidation reaction.

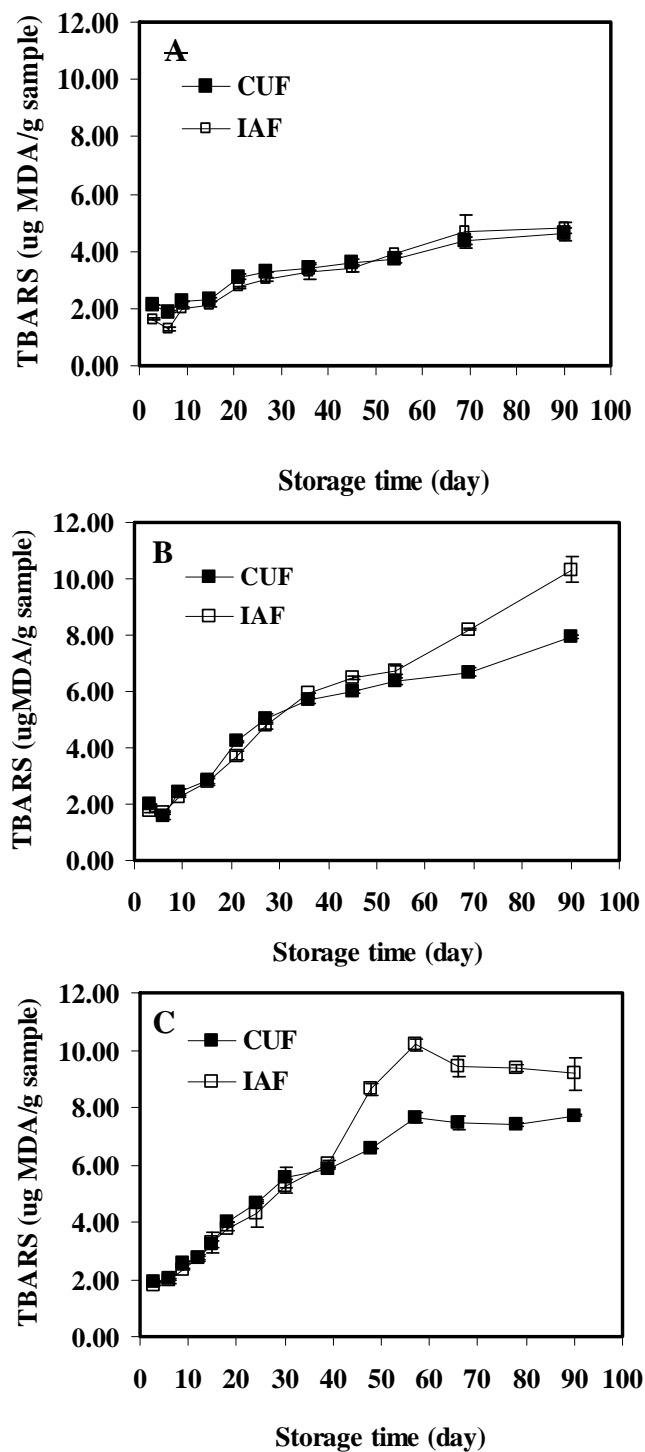


Figure 4.1 TBARS of CUF (commercial use formula) and IAF (Inevitable adding formula) at (A) 35, (B) 45 and (C) 55 °C

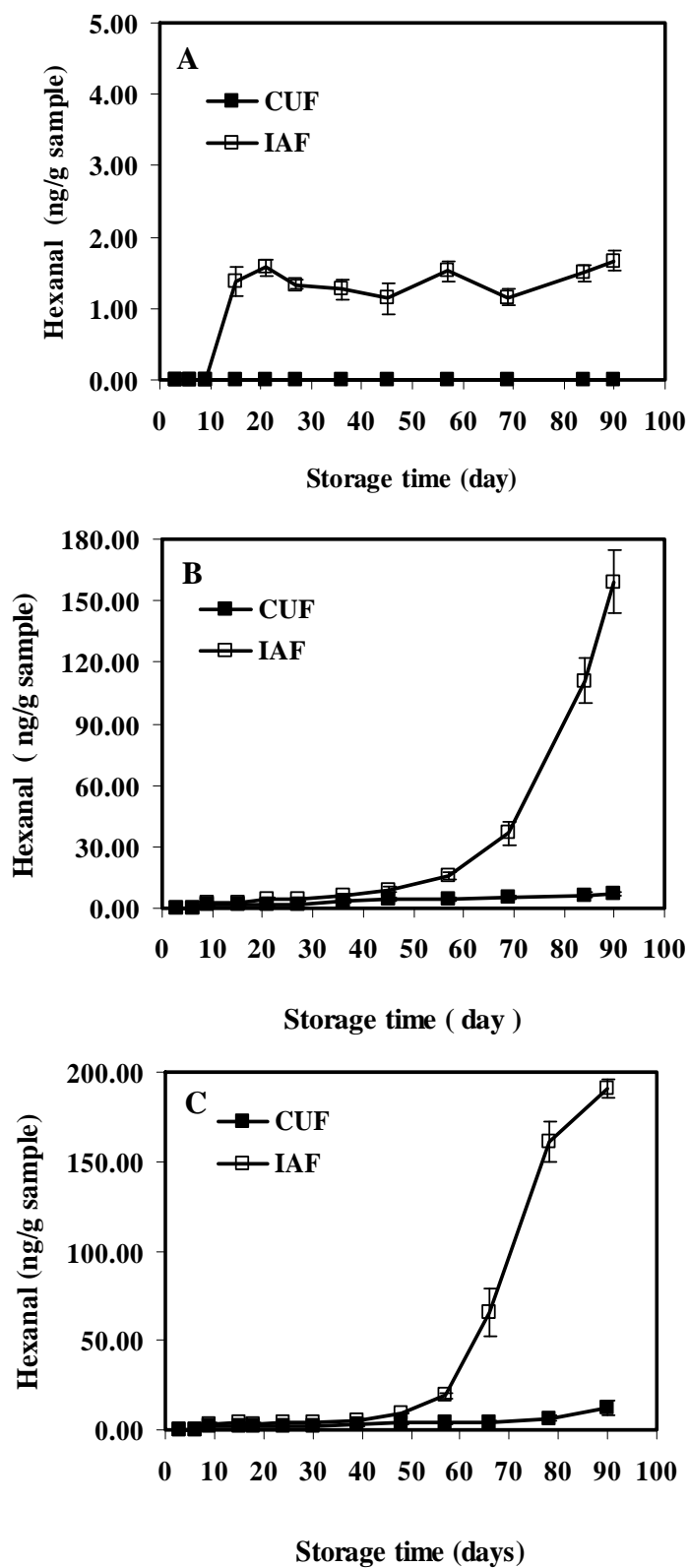


Figure 4.2 Hexanal of CUF (commercial use formula) and IAF (Inevitable adding formula) at (A) 35, (B) 45 and (C) 55 °C

4.4.2 Lipid oxidation of dry food models

Oxidative stability of all commercial dry food models were studied in terms of TBARS and hexanal contents of the products.

4.4.2.1 Dry food model A-H, high protein / fat content

The level of TBARS of dry food model A-H was found to increase with storage time and temperature as shown in Fig. 4.3, but the effect of temperature was less significant when the temperature was higher than 45 °C. A small difference of TBARS contents between the storage temperature of 45 and 55 °C could be a result of further oxidation of aldehyde or other volatile compounds. Moreover, at high temperature storage, small compounds such as propanal and butanal absorbed in plastic bag as a result of low TBARS content. In addition, Maillard reactions could occur at high storage temperature and produced Maillard reaction products leading to increasing the antioxidant activity (Jing and Kitts, 2002; Durmaz and Alpaslan, 2007).

Hexanal contents of all dry food samples were found to be at low concentration range (0.8 – 3.5 ng/g sample) for all storage temperatures (Fig. 4.4). At 45 °C hexanal content was observed since the first week of storage and started decreasing in the 2nd and 4th week when the products were stored at the temperature of 55 and 35 °C, respectively. The fluctuation of hexanal contents was occurred at 45 °C but it gradually increased at the storage time of 55 °C. The hexanal generation data of dry food model A-H showed no significant differences ($p>0.05$) for all storage temperatures. Lower hexanal content could be caused by the oxidation of hexanal into carboxylic acid during storage time (Fennema, 1985) or hexanal bind to the food matrix during storage which was similar to the lipid oxidation of starch extrudates (Gray, Bowen, Farhat and Hill, 2007).

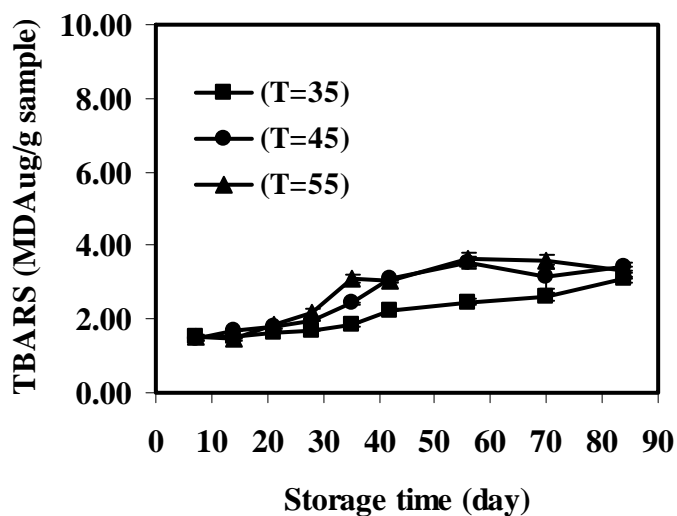


Figure 4.3 TBARS content of dry food model A-H at 35, 45, and 55 °C

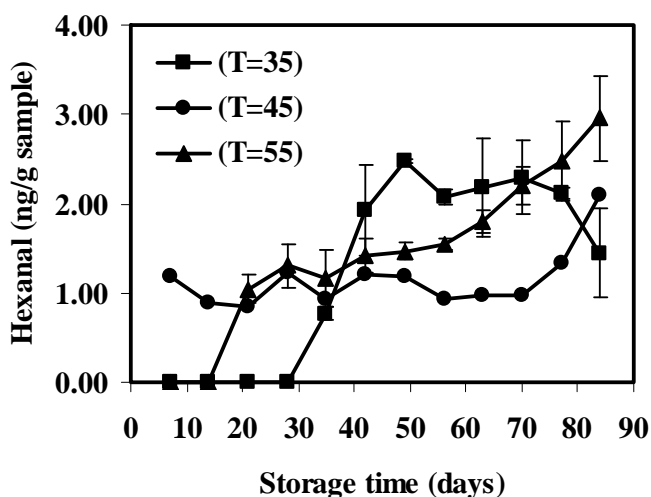


Figure 4.4 Hexanal content of dry food model A-H at 35, 45 and 55 °C

4.4.2.2 Dry food model A

The TBARS of dry food model A increased with storage time as seen in Fig. 4.5. The effect of storage temperature on TBARS contents demonstrated that the amounts of TBARS at 35 °C was lower than 45 °C and 55 °C, but no statistical difference between 45 °C and 55 °C ($p > 0.05$) was found which was similar to result of dry food models A-H. Therefore, TBARS results were unable to differentiate an intensity of lipid oxidation at high temperature range occurring in the extruded dry

food model A-H and A. In addition, due to similarity of formula of CUF and dry food model A could contribute to similar effect of storage temperature on TBARS contents. However, slightly higher TBARS content of the CUF product was observed. This behavior might be due to the effect of production order and storage time of the products prior to be used in the experiment.

Hexanal contents of dry food model A were not found in the 1st week of storage time for all temperature studied, but it started to be detected in the 4th, 2nd and 3rd week for storage temperature of 35, 45 and 55 °C, respectively, as shown in Fig 4.6. A relative steady of hexanal produced for almost 80 days at storage temperature of 35 °C and 45 °C demonstrated that the antioxidant system was able to inhibit lipid oxidation. However, a longer storage time allowed us to see the decline of antioxidant system. In fact, an influence of temperature on the lipid oxidation appeared after eight weeks of storage time, but relatively low level of hexanal content throughout the storage time (less than 2.5 ng/g) suggested a high antioxidant activity. Decrease of hexanal content at the last two weeks of storage time was described by the further oxidation of hexanal or bounding with food matrix.

A comparison of lipid oxidation products between two recipes of dry food model A and A-H is shown in Fig 4.7 (A) and (B). The changing level of TBARS and hexanal content obtaining for the dry food model A-H and A revealed no significant difference all over the storage time, therefore the product recipes had no influence on the intensity of lipid oxidation. Besides, all of the tested samples contained high concentration of BHA/BHT, therefore, the low degree of lipid oxidation was expected for all storage time and temperatures.

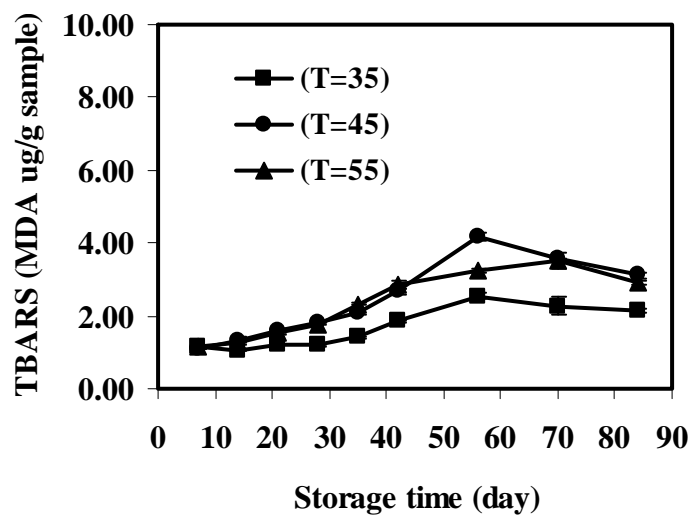


Figure 4.5 TBARS content of dry food model A at 35, 45, and 55°C

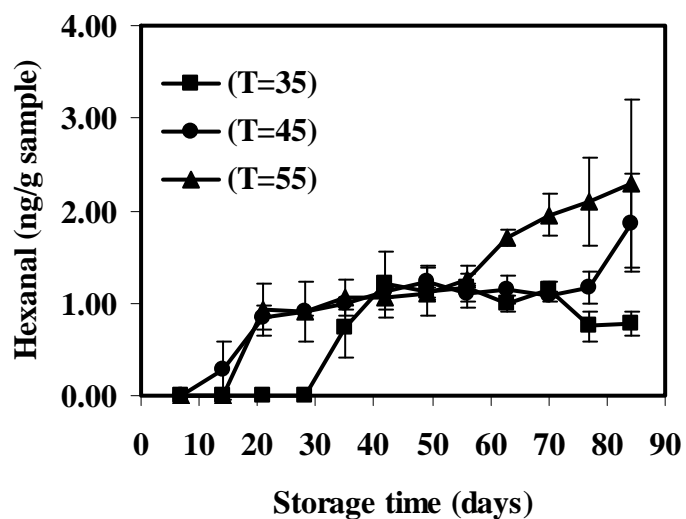


Figure 4.6 Hexanal content of dry food model A at 35, 45, and 55°C

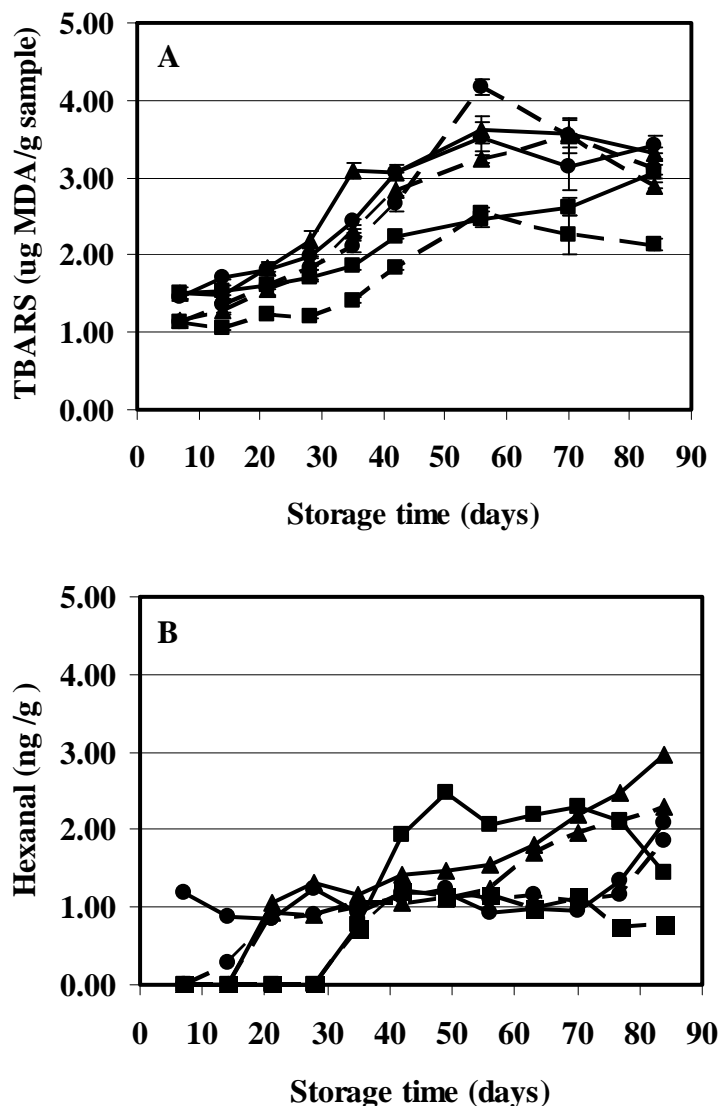


Figure 4.7 A comparison of (A) TBARS and (B) hexanal between (—) dry food model A-H and (---) dry food model A at (■) 35, (●) 45, and (▲) 55 °C

4.4.2.3 Dry food model B-H, high protein / fat content

TBARS of dry food model B-H stored at 35, 45 and 55 °C increased with storage time and temperature as shown in Fig 4.8. As the result of TBARS, it was noticed that at the highest temperature storage (55 °C), the lowest TBARS was observed throughout storage period. The reverse temperature effect found might be

because of an increase of antioxidant efficacy at high temperature due to the contribution of Maillard reaction products (MRP). The MRP could be produced from dry food model B-H ingredients including soy sauce, poultry meal, and fish and meat ingredients which high protein contents along with high temperature storage. Some of the MRP such as reductones and malanoidins are known to have an antioxidant activity (Morales, and Jimenez-Perez, 2001; Yilmaz, and Toledo, 2005; Osada et al., 2006). However, low TBARS content observed at 55 °C could be due to some of the low molecular weight compounds were absorbed in plastic bag and not completely released by directly extraction from food matrix during the determination.

The headspace analysis for hexanal content was determined by drawing the headspace gas from only one bag throughout storage time. Relatively low hexanal contents were detected for all storage temperatures studied as shown in Fig. 4.9. Thus, it could be concluded that temperature and storage time had no effects ($p>0.05$) on the hexanal production of dry food model B-H. Decreasing of hexanal contents during prolong storage could be due to the protective activity of high amounts of antioxidants during production and storage.

TBARS analysis is a tracking for MDA (malondialdehyde) by production of color from the reaction between TBA and aldehydes produced from lipid oxidation. Many factors affecting oxidation include heating temperature during estimation, time, pH, metal ion catalysis and the presence of antioxidants (Bostglou et al., 1994; Chan, 1998). Moreover, other compounds can bind with TBA which could be the reason of increasing TBARS content, while headspace analysis is used to determine only gas phase and high sensitivity with specific volatile compound specially hexanal compound. Although the different TBARS contents between 45 and 55 °C were found, the hexanal contents were showed no significant differences.

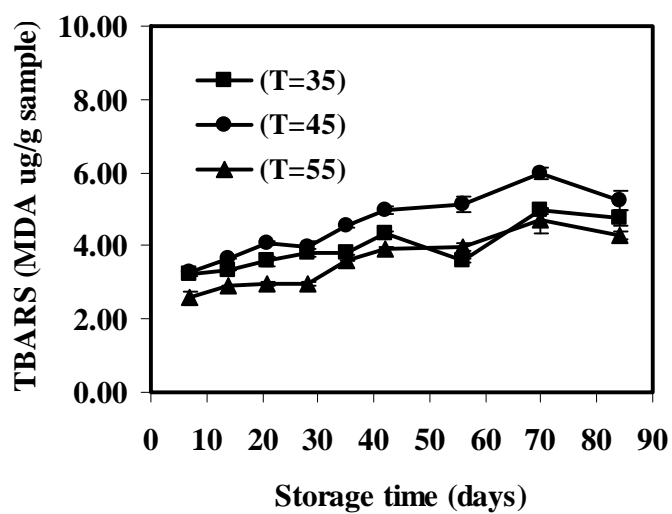


Figure 4.8 TBARS content of dry food model B-H at 35, 45, and 55°C

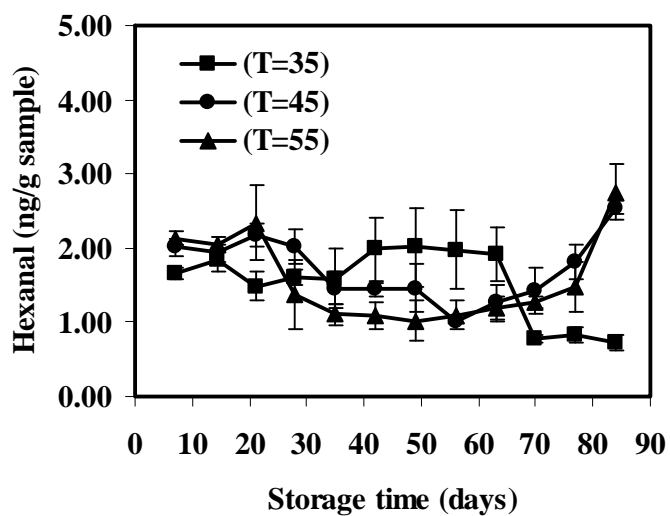


Figure 4.9 Hexanal content of dry food model B-H at 35, 45, and 55°C

4.4.2.4 Dry food model B

Dry food model B had a similar composition with dry food model B-H as shown in Table 4.1. However, other ingredients were added in dry food model B

including sardine head and tail, chicken intestine and chicken head. The TBARS and hexanal contents as the result of lipid oxidation products for dry food model B are shown in Fig. 4.10 and 4.11, respectively. The results demonstrated that TBARS contents slightly increased during storage time and nevertheless, the TBARS contents were not significantly different ($p>0.05$) for all storage temperatures.

The level of TBARS content was unusually found to be an inverse proportion to temperature when the storage temperature was beyond 45 °C. The lowest TBARS content was found at 55 °C, which could be affected by the absorption of low molecular weight compound in plastic film. In addition, it could also be due to the effect of Maillard reactions which delay the lipid oxidation reaction. However, the TBARS was found higher than hexanal content because TBARS determination included all reactive products react which thiobarbituric acid which is not specific only with MDA (Kosugi and Kikugawa, 1985).

Similar to TBARS values, the results of hexanal analysis for dry food model B could provide an affective interpretation of lipid oxidation products as well. Since the hexanal analysis is specific to lipid oxidation reaction, therefore, changing amount of hexanal directly related to an efficiency of BHA/BHT added in the dry food products. No significant differences ($p>0.05$) of hexanal contents throughout the storage periods at the same temperature. However, it was found that hexanal contents of the dry food products were affected by storage temperature ($p<0.01$). The effect of storage temperature on the activity of BHA/BHT indicated that the amounts of BHA/BHT in dry food models were enough for the inhibition of lipid oxidation even for the storage at high temperature. There was no difference of hexanal contents between the storage temperature of 45 and 55 °C was found throughout the storage time. This result supported the inhibition effect caused by other groups of compounds

as mentioned in the TBARS result. On the other hand, the hexanal content was expected to be much higher for the sample stored at 55 °C, if there were no other inhibition mechanisms because of the lipid oxidation was a first order reaction and known to be an increasing function of temperature.

The lipid oxidation of dry food model B-H and B was not different both in terms of TBARS and hexanal content as shown in Fig. 4.12 (A) and (B), respectively. The TBARS contents of both dry food model B-H and B were relative lowest at high storage temperature. This phenomenon might be caused by the contribution of absorbed low molecular weight compounds along with Maillard reactions. However, higher hexanal content of dry food model B-H was found at 45 °C and 55 °C at the end of storage time which revealed the weakening of antioxidant system for dry food model B-H.

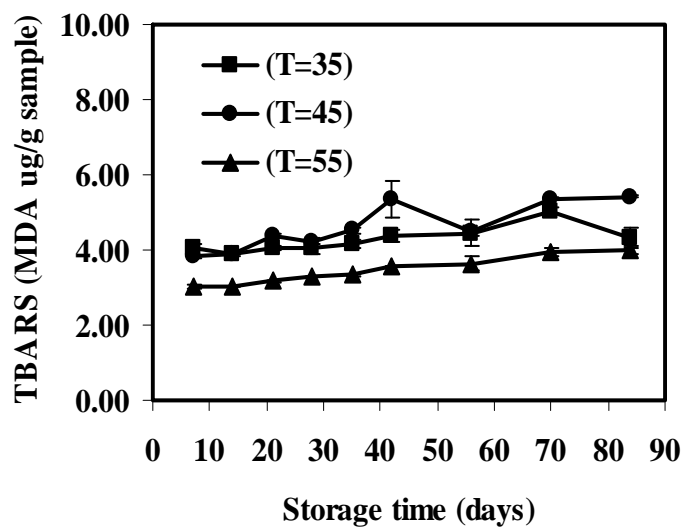


Figure 4.10 TBARS content of dry food model B at 35, 45, and 55°C

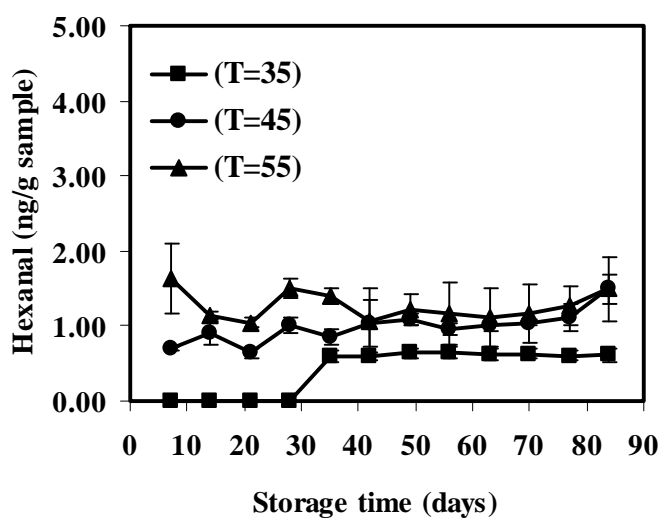


Figure 4.11 Hexanal content of dry food model B at 35, 45, and 55°C

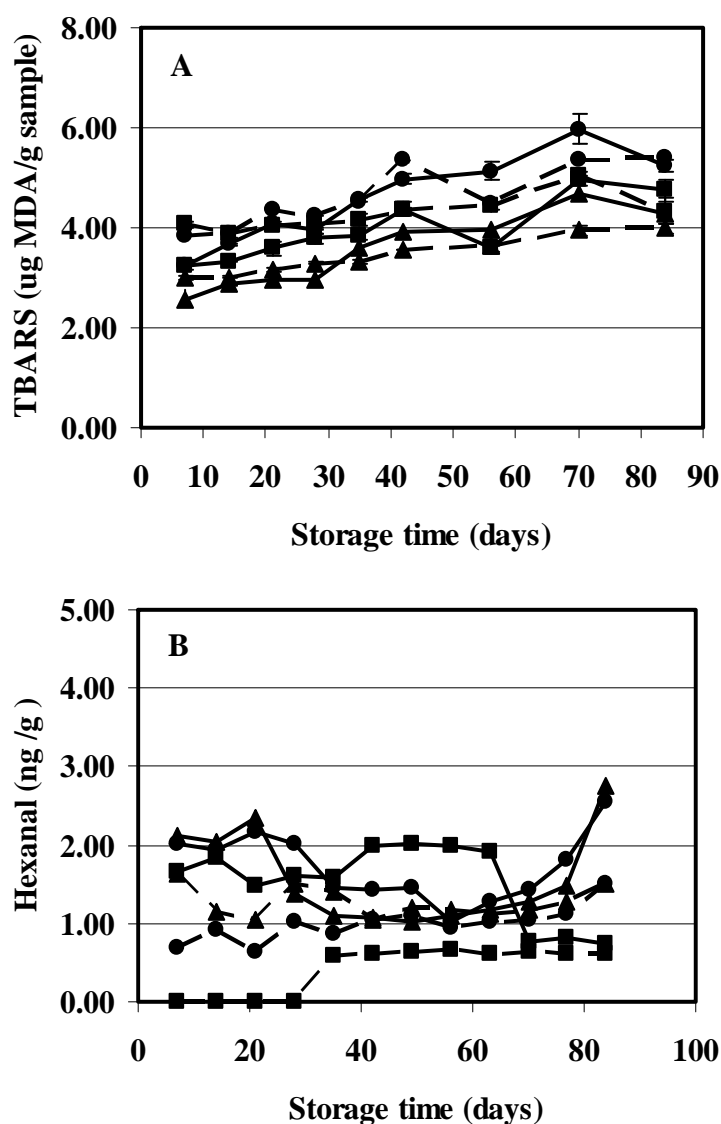


Figure 4.12 A comparison of (A) TBARS and (B) hexanal between (—) dry food model B-H and (- - -) model B at (■) 35, (●) 45, and (▲) 55 °C.

4.4.3 Off-odor evaluation of dry food models

4.4.3.1 Antioxidant efficacy on lipid oxidation of dry food models

The product off-odor was the only sensory attribute evaluated for the experiment of dry food model A and B. The intensity scales were converted into six category scales as barely detectable (1), weak (2), moderate (3), strong (4), very

strong (5) and strongest (6) (Lawless et al., 1998). Off-odor evaluation was done with samples stored for 90 days with 5 sampling times as the results shown in Fig. 4.13 (A) and (B) for CUF and IAF products, respectively, the sample stored at -20 °C was used as control sample for comparing as none or less oxidized intensity. It was observed that increasing of the off-odor intensity a function of storage time for all sample groups.

The off-odor intensity at the same sampling time was also affected by storage temperature which a difference was able to ranking from low to high for 35, 45 and 55 °C. However, the statistical analysis of off-odor intensity revealed that there was no significant difference ($p>0.05$) between the CUF and IAF samples. This could be due to the masking effect of strong odor of the products themselves. It could be suggested that the results of off-odor evaluation of the dry food models were in agreement with the results of chemical analysis. In addition, storing the products under non-light exposure could be one of the factors which gave relatively low lipid oxidation and off-odor intensity (Larsen, Lea, and Rodbotten, 2005; Ibanoglu, Ainsworth, Ozer and Plunkett, 2006). The low hexanal content might be caused by an intermediate water activity level which can delay lipid oxidation (Laseken, et al., 1996).

The hexanal flavor was determined by panelist and found that all panelists could perceive hexanal flavor for IAF sample at 35°C (90 days), 45 °C (45 days) and 55 °C (45 days). It was also observed that the CUF product has lower hexanal content than did the IAF product. The off-odor intensity for CUF and IAF samples was considered moderate to very strong off-odor for all storage temperatures.

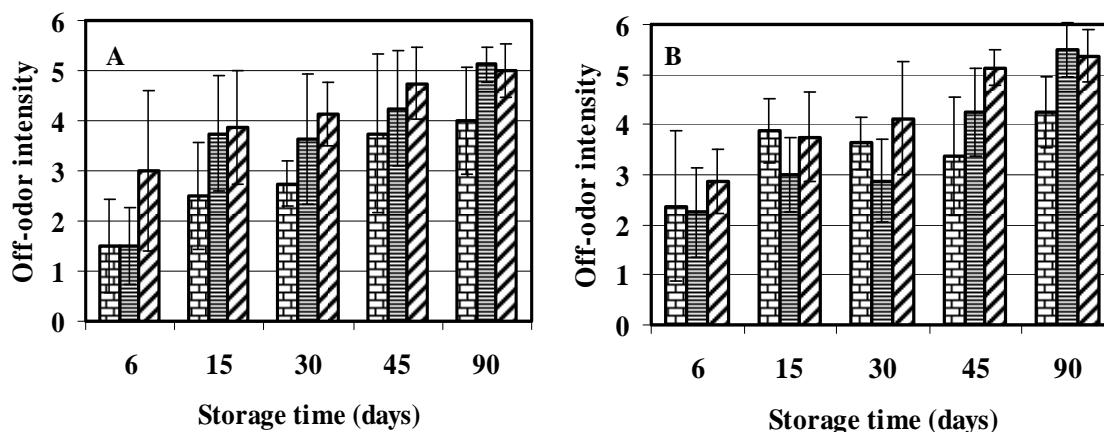


Figure 4.13 Off-odor evaluation of dry food model A for CUF (commercial use formula) (A) and IAF (Inevitable adding formula) (B) sample at (▤) 35°C, (▥) 45 °C and (▧) 55 °C.

4.4.3.2 Off - odor evaluation of dry food models

Sensory evaluation of dry food model A-H and model A at 35, 45 and 55 °C are demonstrated in Fig. 4.14 (A) and (B), respectively. The sensory evaluation of dry food model A-H at storage temperature of 35 °C had lower off-odor intensity than those stored at 45 and 55 °C in the first 2 weeks of storage time. The products stored at 45 °C gave off-odor intensity similar to those stored at 55 °C for all storage time. It was also found that off-odor intensity of the products stored at 35 °C was less than those stored at 45 and 55 °C. Thus the off-odor evaluation at 45 and 55 °C were agreed with chemical analysis for both dry food model A-H and A as described previously. In addition, off flavor characteristic of dry food model A-H was not like hexanal odor but the flavor was relatively similar to hexanal for samples stored towards the end of storage time at high temperature.

Slightly different off-odor intensity due to the storage time was observed for dry food model A stored at 35, 45 and 55 °C, but the effect of temperature was illustrated no significant difference ($p > 0.05$). The effect of storage temperature on

sample off-odor was not found in these dry food models which similar to the results reported by Larsen et al. (2005) for the off-odor of extruded oat stored at 23 and 38 °C for 3 and 10 months. In addition, no different off-odor intensity was found which could be due to the masking effect of other compositions.

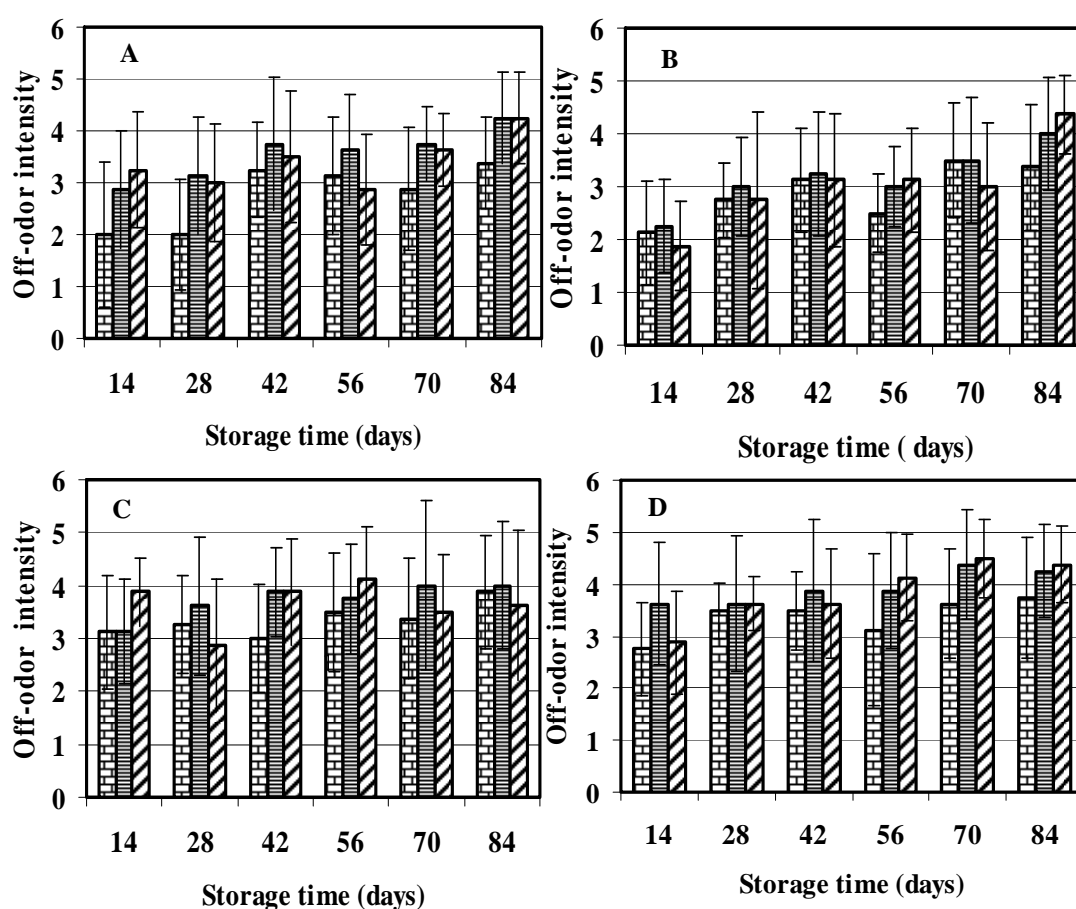


Figure 4.14 Off-odor intensity for dry food models (A), model A-H, (B) model A, (C) model B-H and (D) model B at (▤) 35 °C, (■) 45 °C and (▨) 55 °C

The off-odor intensity of dry food model B-H at 35, 45 and 55 °C were in agreement with TBARS and hexanal results. The off-odor intensity was not significantly different ($p > 0.05$) and found for all storage temperatures (Fig. 4.14 C). For the off-odor intensity of dry food model B was found to be constant when

compared between experienced and controlled samples (sample stored at -20°C) as shown in Fig. 4.14 (D), these results were similar to dry food model B-H.

The off-odor results indicated the effect of different ingredient between dry food model A and B. Higher off-odor intensity was found for both dry food model B than model A. The off-odor intensity of dry food model A and A-H were rated as moderate to strong while dry food model B-H and B were moderate to very strong off-odor.

4.4.3.3 Correlation between sensory evaluation and chemical analysis

In order to set the rejection level of off-odor of the dry food products used in this experiment correlated with TBARS and hexanal contents. From sensory evaluation of the products, Hexanal flavor was detected by all panelists at the temperature of 35°C for 90 days and 45 days for 45°C and 55°C . Thus, the lowest level of perception of the panelists at low temperature was selected for setting rejection level and used as a tool for making decision during storage or product monitoring. The rejection level of hexanal and TBARS were set by chemical analysis at storage temperature of 35°C for 90 days as shown in Table 4.2 and 4.3 for hexanal and TBARS, respectively.

Table 4.2 Hexanal content (ng/g sample) of dry food models at 35, 45 and 55 °C

Dry pet foods	Hexanal (ng/g sample)		
	35 °C	45 °C	55 °C
IAF (Inevitable adding formula) (90 days)	1.671± 0.15	159.342±15.09	190.934 ± 5.23
CUF (Commercial use formula) (90 days)	0.001± 0.00	6.996± 1.25	6.601 ± 1.37
Model A (84 days)	0.778 ± 0.14	1.868 ± 0.52	2.282 ± 0.91
Model A-H (84 days)	1.448 ± 0.50	2.092 ± 0.60	2.955 ± 0.48
Model B-H (84 days)	0.729± 0.11	2.551± 0.08	2.752 ± 0.38
Model B (84 days)	0.610 ± 0.09	1.502 ± 0.19	1.496 ± 0.42

Table 4.3 TBARS content (MDA ug/g sample) of dry food models at 35, 45 and 55 °C

Dry food models	TBARS (MDAug/g sample)		
	35 °C	45 °C	55 °C
IAF (Inevitable adding formula) (90 days)	4.801 ± 0.20	10.328 ± 0.44	9.166 ± 0.55
CUF (Commercial use formula) (90 days)	4.604 ± 0.22	7.930 ± 0.05	7.729 ± 0.04
Model A (84 days)	2.135 ± 0.07	3.125 ± 0.08	2.897 ± 0.04
Model A-H (84 days)	3.078 ± 0.09	3.423 ± 0.12	3.318 ± 0.08
Model B-H (84 days)	4.749 ± 0.21	5.253 ± 0.27	4.269 ± 0.11
Model B (84 days)	4.338 ± 0.26	5.419 ± 0.02	3.991 ± 0.11

The rejection level of hexanal content was set at 1.671 ng/g for the product stored at temperature of 35 °C and all dry food models studied had lower hexanal contents than the rejection level. Storage at 45°C and 55 °C, the products had higher hexanal content than rejection level due to increasing of lipid oxidation which found both of dry food model A and model B. However, hexanal contents at high temperatures were slightly different from the rejection level. In addition, the rejection level for TBARS

was set at 4.8 ug MDA/g which was the content of IAF sample at 35 °C stored for 90 days. Most of dry food models contained lower TBARS contents than the rejection level as shown in Table 4.3 which the dry food model A contained the lowest value. Nevertheless, the hexanal rejection level set in this experiment was shown to be lower than the value set for other food products including extruded oat cereal with high phenolic compounds stored at 35 °C and cooked ground pork-(Viscidi et al., 2004; Juntachote, Berghofer, Siebenhamdl and Bauer, 2007).

4.4.3.4 Lipid oxidation of dry food models stored in actual storage condition

The experimental results of dry food model A-H A, B-H and B. stored at 32 °C for the period of 18 months are shown in Fig. 4.15 A-D, respectively. TBARS content for dry food model B-H and B slightly decreased with increasing storage time while constant TBARS were found both of model B-H and A throughout storage time. For dry food model B, TBARS decreased at the first few months of storage while constant TBARS were found for both model B-H and B. However, TBARS of both dry food model A tended to be lower than dry food model B because of difference in their compositions especially source of fat content which responsible to the degree of lipid oxidation. Actual or commercial storage condition in this study had lower TBARS content than those of accelerated ones as described previously due to lower storage temperature. The longer storage time (18 months) under dark condition and packaging materials of non gas type barrier could provide the loss of volatile compounds.

Hexanal contents were not found for all dry food models in this study because their quantity might be less than the lower detection limit. For the reason that hexanal is a volatile compound thus it can be lost during storage, in company with none gas type barrier of plastic bag. The actual or commercial condition testing was set at 32 °C

which relatively lower storage temperature than the lowest temperature of acceleration test. For the reason that at temperature of 32 °C was inappropriate for predicting lipid oxidation rate of all commercial dry food models. According to actual or commercial testing, lipid oxidation of commercial dry food models were not affected by room temperature storage and fewer risks in odor changing (off-odor). Amounts of odor changing depend on type of lipid, antioxidant, other dry food ingredients and storage conditions.

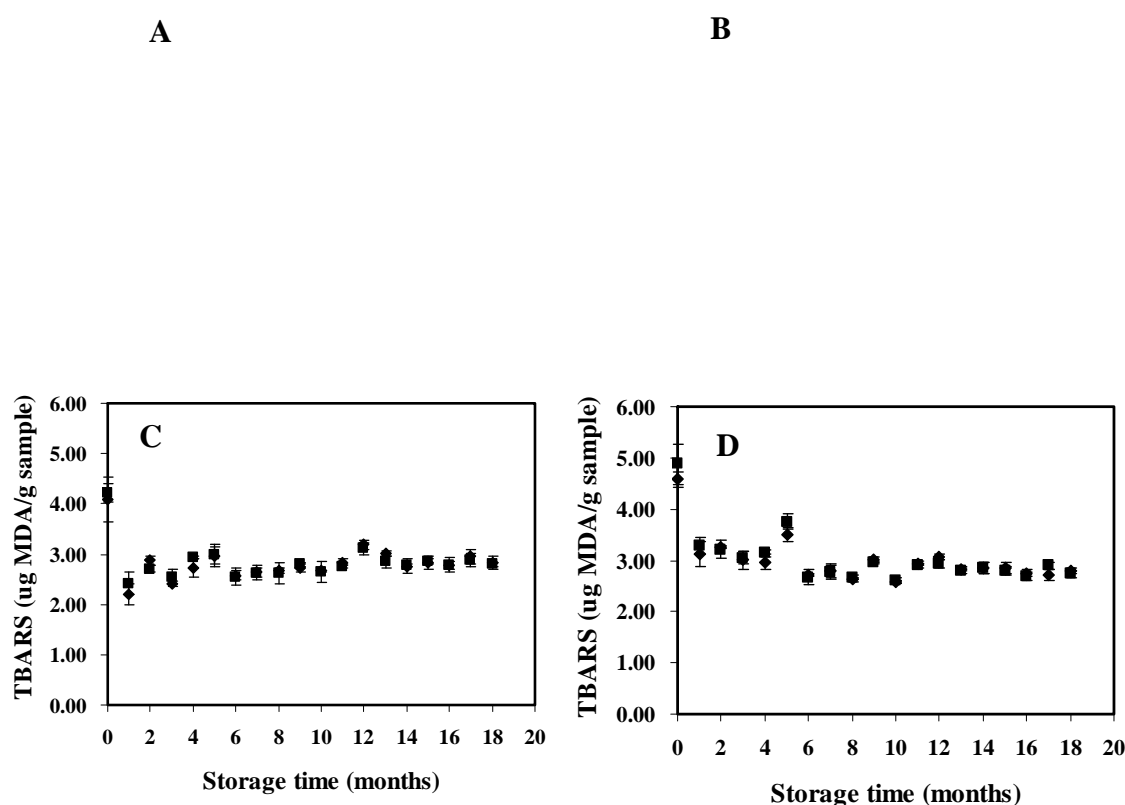


Figure 4.15 TBARS content of dry food model (A) model A-H, (B) model A, (C) model B-H and (D) model B at 32 °C for 18 months.

4.4.3.5 Kinetic reaction rate of dry food models

The kinetic reaction rate of lipid oxidation was determined only for dry food model A. In addition, the kinetic reaction rates of CUF and IAF samples were served as a tool for computing the maximum level of lipid oxidation products. These

products were specially processed by removing antioxidants or inevitable adding BHA/BHT (IAF sample) and commercial use formula with high concentration of BHA/BHT (CUF sample). The kinetic reaction rates (k) were increased with temperatures which calculated by from hexanal and TBARS contents as shown in Table 4.4. The activation energy of TBARS was lower than that of hexanal but both of activation energy were relatively lower when compared with activation energy of edible oil (24-240 kJ/mol) (Colakoglu, 2006).

The reaction rate constant of IAF at 35, 45 and 55 °C were used as references for estimating the quality of other dry food models in this experiment. The lipid oxidation evaluation was calculated from hexanal contents as presented in Fig 4.16 at the temperature 35, 45 and 55 °C, respectively. At the temperature of 35, 45 and 55 °C, low lipid oxidation for CUF sample was observed and the same for dry food model A throughout storage time. Hexanal contents of all dry food models had lower kinetic reaction rate than that of milk (thermal treatment) stored at 45 °C ($k=0.01 - 0.1 \text{ min}^{-1}$) and 55 °C ($0.012 - 0.106 \text{ min}^{-1}$), an activation energy 35.2 kJ/mol (Vazquez-Landaverde, 2007). The effect of antioxidant added on reaction rate was similar to the lipid oxidation of poultry meat which TBARS was inhibited by natural antioxidant at storage temperature of 4 °C (Barretto, Ida, Silva, Torres, and Shimokomaki, 2003).

Table 4.4 Reaction rate constant (k) and activation energy (E_a) of IAF (Inevitable adding formula)

Temperature (°C)	Hexanal		TBARS	
	k (day ⁻¹)	E_a (kJ/mol)	k (day ⁻¹)	E_a (kJ/mol)
35	0.0212	65.64	0.0270	28.69
45	0.0474		0.0383	
55	0.1011		0.0533	

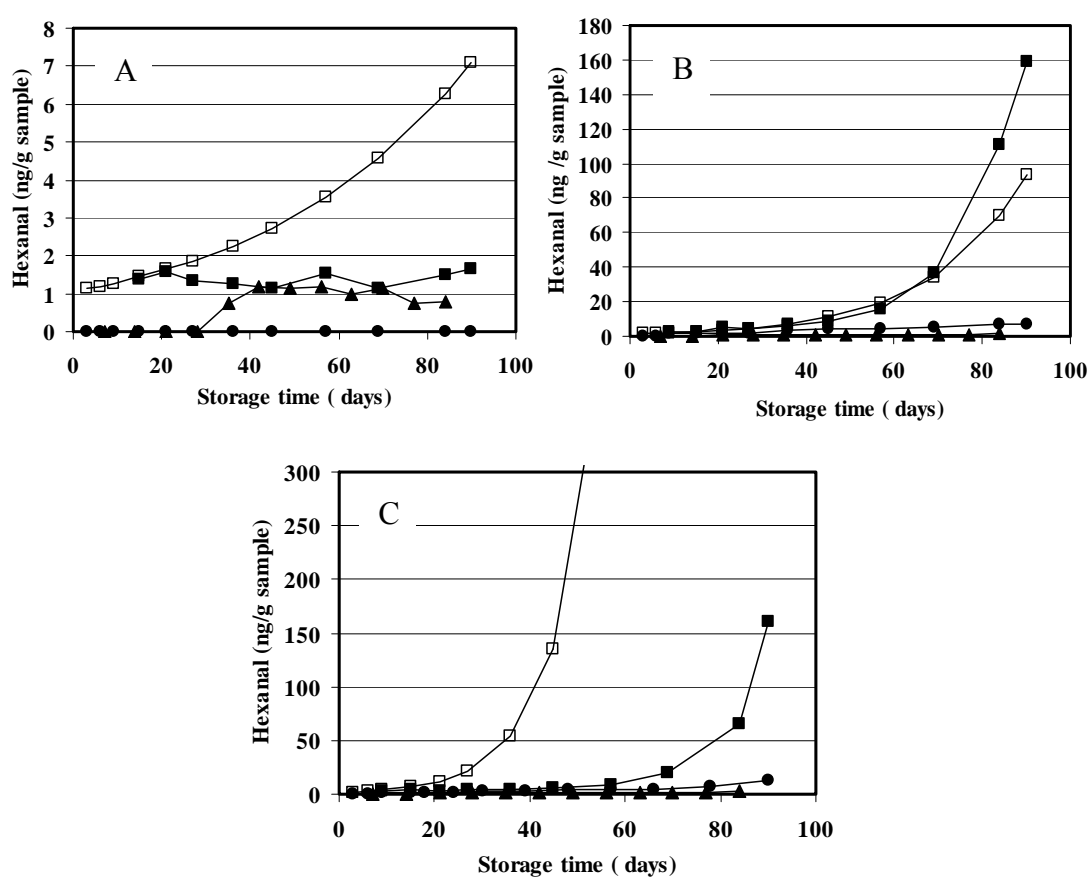


Figure 4.16 Hexanal content comparison between calculated using kinetic reaction rate (□), CUF (commercial use formula) (●) and IAF (Inevitable adding formula) (■) samples and dry food model A (▲) at 35 (A), 45 (B) and 55 °C (C).

4.5 Conclusions

Low lipid oxidation of all dry food models used for this study was observed throughout storage time. The product made with inevitable adding formula (IAF) had higher TBARS and hexanal content than did the commercial use formula (CUF) for all storage temperatures. TBARS and hexanal contents of all dry food models increased with increasing temperature and storage time. Low hexanal content was found for all dry food models. Off-odor of all dry food model studied was not significantly different between storage temperatures. For long term storage, it could be concluded that antioxidant effectively inhibited oxidation of the dry food models used in this study. The rejection level of TBARS and hexanal contents were set at 4.8 ug/g and 1.671 ng/g, respectively. The kinetic reaction rate was calculated using inevitable adding formula products which reaction rate increased with temperature. Low oxidation of all dry food products was found although they were kept at high temperatures.

4.6 References

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CHAPTER V

SUMMARY

Moisture sorption isotherm of tested dry food models, that were divided by protein into two types (dry food model A and B), besides each of dry food model was sub grouped as a normal and high protein/fat content. All of the studied dry food models also had a different physical property including shape and size of their kibble. The moisture adsorption and desorption isotherms of all testing product, was represented by a type II isotherm (S-shape). At constant temperature, the equilibrium moisture content (EMC) was increased with an increasing level of water activity. Besides that the EMC was an inverse function of temperature at constant water activity for all of the testing food models. The effect of high protein and fat content on moisture sorption isotherm was found for both types of dry food models. For the same type of dry food model, the profile for desorption isotherm was lied above the adsorption isotherm or the hysteresis phenomena was exiting. However, the hysteresis was hardly noticed at the highest storage condition for all of testing cases, because water molecules at a high energy state tend to escape form sorption sites. The hysteresis phenomenon indicated the irreversible changes of their structure and hygroscopic property of these dry food models. The GAB model provided the best fit to experimental data of sorption isotherms with a higher value of R^2 and lower MRE, RSS and SEE comparing to another isotherm models. Monolayer moisture content, (M_0) of every testing product was obtained by BET model and the M_0 for all cases

exhibited the temperature independence. Comparison of M_0 between dry food models A and B showed no significant difference. Therefore, the recipes and physical property had no influence on the monolayer moisture sorption. Thermodynamic properties involved with the moisture sorption process. Thermodynamic properties of dry food models studied were obtained, the isosteric heat of sorption or differential enthalpy of sorption was a non-linear decreasing function of product's equilibrium moisture content. The isosteric heat of moisture desorption process was lied above the one for adsorption process because the equilibrium moisture content at a given water activity for desorption isotherm sample was always higher than the one for adsorption sample. Entropy of sorption decreased with an increasing of moisture content. The entropy function demonstrated the available of sorption site was lower at higher moisture content. Unlike the moisture sorption isotherm, the different of sorption entropy between dry food models A and B were identified due to different of their protein source and remaining ingredients. According to moisture sorption isotherm studied, the moisture sorption isotherm and thermodynamics properties of all dry food model studied were used for predicting the physical property especially for the textural change during storage and transportation.

Lipid oxidation was evaluated by accelerated testing method at storage temperature of 35, 45, and 55 °C. The studies were conducted for all types of the dry food models similar to what were used in the moisture sorption experiments. The effect of antioxidant added on inhibition of lipid oxidation was studied by using two special groups of type A-food model, namely the commercial use formula sample (CUF or full load of BHA and BHT) and inevitable adding formula sample (IAF contained 0.0064% of BHA/BHT in CUF sample). The CUF sample had lower levels

of TBARS and hexanal than the IAF sample for the same storage temperatures. TBARS and hexanal contents of all the testing dry food models were increased with storage time and temperature. Off-odor evaluation of CUF and IAF samples were slightly increased with storage time and temperature, the off-odor of the IAF sample alone was also noticed as hexanal alike odor. On the other hand, the hexanal alike odor in the IAF sample confirmed that the lipid oxidation played an important part in the off-odor process. For a long term storage condition, at 32 °C for 18 months, studied results revealed a relatively low level of TBARS and no detection of hexanal throughout the storage time. The low rate of lipid oxidation determined for the long term storage was due to low initial level of moisture content together with a small change of moisture contents and enough amount of antioxidant for slowing down the lipid oxidation during storage time. The off-odor rejection level of TBARS and hexanal for all dry food models were determined to be at 4.8 µg/g and 1.67 ng/g, respectively. The kinetic rates of lipid oxidation reaction were obtained for the IAF samples and the activation energy of TBARS and hexanal were at 28.69 and 65.64 kJ/mol, in that order.

BIOGRAPHY

Piyaporn Neamsungnoen was born in October 18th, 1982 at Nakhon Ratchasima, Thailand. She studied her high school diploma at Kudjig Wittaya School (1995-1997) and Nakhon Ratchasima Wittayalai School (1998-2000). In 2004, she received the degree of Bachelor of Science (Food Technology) from Suranaree University of Technology, Nakhon Ratchasima, Thailand. During study, she participated in the food scientist competition “FOSTAT-Nestle Quiz Bowl 2003”. She started to study for her Master degree in Food Technology at Suranaree University of Technology, Nakhon Ratchasima, Thailand. During graduate study, she was a teaching assistant in the food quality control laboratory and the food engineering. The results from her research were also presented in several articles including;

Moisture sorption isotherm of dry pet food in the 8th Agro-Industrial Conference, 15th-16th, June, 2006, Bangkok, Thailand.

Thermodynamics approach for describing moisture sorption isotherm of dry pet food in the International Conference on Engineering, Applied Science and Technology, 21st-23rd, November, 2007, Bangkok, Thailand.