PESTICIDE RESIDUES DEGRADATION OF DRIED CHILI BY GASEOUS OZONE FUMIGATION

PANLOP SINTUYA

DOCTOR OF ENGINEERING IN FOOD ENGINEERING
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A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF ENGINEERING
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ชื่อเรื่อง การสลายตัวของสารตกค้างยาฆ่าแมลงในพริกแห้งโดยวิธีการรมแก๊สโอโซน
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บทคัดย่อ

ปัจจุบันการทำเกษตรกรรมมีการใช้ยาฆ่าแมลงในปริมาณที่สูงมาก จึงส่งผลให้ผลิตผลทางการเกษตรมีการปนเปื้อนของสารตกค้างยาฆ่าแมลง การรมแก๊สโอโซนเป็นเทคนิคที่ช่วยลดปริมาณสารตกค้างยาฆ่าแมลงได้ งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาผลกระทบของการรมแก๊สโอโซนต่อการเสื่อมสลายของสารตกค้างยาฆ่าแมลงและคุณภาพของพริกแห้ง ในการทดลองได้ทำการศึกษาการสลายตัวของของสารตกค้างยาฆ่าแมลง 6 ประเภท ได้แก่ daizinon malathion chlorpyrifos prefenofos ethion และ triazophos นอกจากนี้ยังได้ศึกษาจลนพลศาสตร์ของการสลายตัวของสารตกค้างยาฆ่าแมลง ค่าการสลายตัวครึ่งชีวิต ($t_{1/2}$) และคุณภาพด้าน ต่าง ๆ ของพริกแห้ง ได้แก่ ปริมาณสารประกอบฟีนอลิก สารต้านอนุมูลอิสระ ปริมาณน้ำอิสระ สี และปริมาณสาร capsaicin และสภาพกายภาพของพื้นผิวพริกแห้งหลังการรมแก๊สโอโซน จากการวิจัยพบว่า หลังการเก็บรักษาผลิตภัณฑ์พริกแห้งเป็นระยะเวลา 8 วัน ปริมาณของสารตกค้างยาฆ่าแมลงทั้ง 6 ประเภท มีการสลายตัวตามธรรมชาติอยู่ในช่วง 28-46% โดยสามารถคำนวณค่าการสลายตัวครึ่งชีวิต ($t_{1/2}$) ได้อยู่ในช่วง 66.6-120.9 วัน เมื่อทดสอบรมพริกแห้งด้วยแก๊สโอโซนเป็นระยะเวลา 30 นาทีแล้ว พบว่าการสลายตัวของสารตกค้างยาฆ่าแมลงเร็วขึ้น อยู่ในช่วง 45-69% คิดเป็นค่า $t_{1/2}$ อยู่ในช่วง 17.4-32.1 นาที เมื่อเปรียบเทียบค่า $t_{1/2}$ ของการสลายตัวตามธรรมชาติแล้ว การรมโอโซนสามารถเพิ่มอัตราการสลายตัวของสารตกค้างยาฆ่าแมลงได้เร็วกว่าถึง 99.9% นอกจากนี้ยังพบว่า การรมแก๊สโอโซนไม่ส่งผลต่อลักษณะพื้นสัมผัสของพริกแห้ง ปริมาณสารประกอบฟีนอลิก สารต้านอนุมูลอิสระ ปริมาณน้ำอิสระ สี และปริมาณสาร capsaicin อย่างมีนัยสำคัญ ($p \geq 0.05$)

ในส่วนที่สองของงานวิจัยได้มีการศึกษาการรมแก๊สโอโซนด้วยระบบหมุนเวียนอากาศแบบบังคับ (VFA) โดยได้ศึกษาในรูปแบบของตัวแปรไร้มิติ โดยได้ประยุกต์ใช้ทฤษฎี Buckingham PI เพื่อศึกษาความสัมพันธ์ของตัวแปรไร้มิติ พบว่าค่า Reynolds number มีความสัมพันธ์กับ ค่า Hydraulic diameter และพบว่าการรมแก๊สโอโซนด้วยเทคนิค VFA สามารถลดปริมาณของ chlorpyrifos อยู่ในช่วง 49-71% ตลอดช่วงความหนาของชั้นตะกร้าที่บรรจุพริกแห้ง อีกทั้ง การรม

โอโซนด้วยเทคนิค VFA สามารถเพิ่มประสิทธิภาพการลดยาฆ่าแมลง 28% และลดต้นทุนการดำเนินงานได้มากถึง 34% เมื่อเทียบกับการรมโอโซนธรรมดา โดยความสัมพันธ์ของค่าการสลายตัวของปริมาณสารตกค้างยาฆ่าแมลงกับตัวแปรไร้มิติสามารถนำไป Scale-up ในรูปแบบของชั้นความสูงของตระกร้า อัตราการไหลของอากาศผ่านตะกร้าพริก และความดันตกคร่อม เพื่อเป็นประโยชน์ในการออกแบบห้องรมแก๊สโอโซนด้วยเทคนิค VFA สำหรับลดปริมาณยาฆ่าแมลงตกค้างในพริกแห้ง ในระดับอุตสาหกรรมต่อไป

คำสำคัญ : โอโซน, สารตกค้างยาฆ่าแมลง, ค่าการสลายตัวครึ่งชีวิต, จลนพลศาสตร์ของการสลายตัว, ระบบหมุนเวียนอากาศแบบบังคับ

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ABSTRACT

Due to the excessive uses of pesticide in the current agricultural farming, the products are normally contaminated with pesticide residue. Gaseous ozone fumigation is the technique that could reduce pesticide efficiently. The objective of this work was to study the effects of ozone fumigation on pesticides residue degradation in dried chili and to study the potential of scale up on ozone application. The first part was conducted by studying the degradation of 6 pesticides, namely, diazinon, malathion, chlorpyrifos, prefenofos, ethion and triazophos. The study also determined the degradation kinetics of pesticide residues, degradation half-life period ($t_{1/2}$), and dried chili qualities. This includes, total phenolic compounds, antioxidant properties, water activity, color, capsaicin content and physical property of chili surface after gaseous ozone fumigation treatment. Results showed that, after 8 weeks of storage, the of pesticides were naturally degraded in the range of 28-46% with the $t_{1/2}$ in the range of 66.6-120.9 days. After dried chili was fumigated with gaseous ozone for 30 min in a pressurized tank, pesticide residue exhibited the degradation in the range of 45-69% with the $t_{1/2}$ in the range of 17.4-32.1 min. Compared to the natural degradation, the ozone fumigation is better and more effective to degrade the pesticide by 99.9%. Furthermore, ozone fumigation didn’t significantly affect ($p \geq 0.05$) chili surface morphology, total phenolic compounds, antioxidant properties, water activity, color and capsaicin content of dried chili.

In second part, the vertical force air circulation (VFA) was applied to the ozone fumigation process and the study of dimensionless parameters to determine the potential of system scale up was conducted. The Buckingham PI –

theorem was applied to obtain dimensionless parameters of the VFA fumigation analysis. It was found that, the Reynolds number (Re) corelated with hydraulic diameter and pressure drop. The reduction of chlorpyrifos residue under gaseous ozone fumigation using VFA technique was in a range of 49-77% throughout the vertical stacking column of chili. Moreover, ozone fumigation with VFA was able to improved the ozone fumigation on degradation efficiency by 28% and save operation cost by of 34% compared to conventional ozone fumigation. The relationship between pesticide residue degradation and dimensionless parameters could be used for commercial scale-up in terms of stacking height, air flow rate throughout chili basket, and pressure drop. The findings from this study provide benefit of the gaseous ozone fumigation to reduce the pesticide degradation in dried chili with VFA system that can be scale-up for the commercial application.

Keywords : Ozone, Pesticide residues, Degradation half-life, Degradation kinetic, Vertical forced-air circulation (VFAC)

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CHAPTER 1
INTRODUCTION

1.1 Background of Research

Thailand is known as a major exporter for agricultural products to in the world (Panuwet et al., 2012). A demand for world agricultural products has been increasing due to the growth of world population. For example, according to rice demand outlook by the United States Department of Agriculture (USDA), world rice consumption in 2017 is predicted to be 480.1 million tons per year, which increased by 1.4 million tons from 2016 (Popp et al., 2013; USDA, 2017). Due to a limitation of farm land, farmers have to increase their crop yield on existing farmland to reach the demand (Popp et al., 2013). However, pests and farming efficiency is a major cause of crop losses that obstacts the farming efficiency. In order to control crop pests in agriculture and to minimize crop losses, the use of pesticides in Thailand has been increasing extensively over time (Blankson et al., 2016; Oerke and Dehne, 2004; Ooraikul et al., 2011; Panuwet et al., 2012). Consequently, pesticide residues are detected in most Thai agricultural products as a result of the high pesticide application rates (Harnpicharnchai et al., 2013). Since organophosphate is highly effective and inexpensive, it is one of the most popular pesticides that is generally used in Thailand (Harnpicharnchai et al., 2013; Ooraikul et al., 2011). Nevertheless, organophosphate is highly toxic. It is harmful to human by causing health problems such as respiratory, myocardial, and neuromuscular transmission impairments (Chowdhury et al., 2012; Clarke et al., 1997; Damalas and Eleftherohorinos, 2011; Duangchinda et al., 2014; Issa et al., 2010; Oerke and Dehne, 2004; Ooraikul et al., 2011; Wilson and Tisdell, 2001).

Chili is an important agricultural product of Thailand. It is used as basic ingredient in daily cooking all over the world. Thailand produces a large number of chili and exports it as the fresh, sauce and dried chilies. The amount of exporting chili increases every year (Kaewkiew et al., 2012; Nathakaranakule et al., 2006). From the previous report, it was found that organophosphate pesticide residues were detected in chili crop (Ooraikul et al., 2011). Therefore, it is essential to develop an efficient method for removing or reducing the pesticide residues of chili in order to meet the safety and quality standards of exporting agricultural products. There are several techniques have been reported to reduce pesticide residues such as ozone fumigation (Botondi et al., 2015; Gabler et al., 2010; Heleno, Fernanda F. et al., 2014; Msayleb and Ibrahim, 2011), UV photolysis (Chelme-Ayala et al., 2010; Garbin et al., 2007; Kowalska et al., 2004; Zhang et al., 2008), semiconductor photocatalysis (Hashimoto et al., 2016; Hurum et al., 2003; Lannoy et al., 2017), electrochemical oxidation (Guelfi et al., 2016; Rubí-Juárez et al., 2016), and Fenton oxidation (Saini et al., 2016; Sedaghat et al., 2016). However, none of them has been reported to be used on dried chili.

Ozone fumigation is one of the most prominent technique that produce no secondary pollutants (Botondi et al., 2015; Chen et al., 2013). The by - product of ozone is oxygen. Thus, it does not releases toxic residues on treated product (Botondi et al., 2015). In this work, gaseous ozone fumigation is proposed to degrade organophosphate pesticides on dried chili. The degradation kinetic, water activity, color and capsaicin content of dried chili after fumigated with ozone was investigated. Then, conceptual design of gaseous ozone fumigation was developed for pesticide degradation in dried chili using a novel forced-air circulation technique.

1.2 Objectives of Research

The objective of this research was to develop the ozone fumigation process on dried chili for pesticide residue degradation which consists of 2 minor objectives stated below:

1. To study the pesticides degradation efficiency on dried chili under gaseous ozone fumigation and the effect of gaseous ozone fumigation to physical and chemical properties of dried chili.
2. To develop gaseous ozone fumigation on dried chili using a novel forced-air circulation technique.

1.3 Scope of the Research

1. Dried chili samples free from pesticide residue contamination was obtained from local market in Chiang Mai Thailand.
2. Degradation of organophosphate pesticide residue in dried chili by ozone fumigation is determined. Ozone fumigation process which affect to pesticide degradation but not affect to chemical and physical is obtained.
3. The prototype of force-air circulation chamber for pesticide degradation by gaseous ozone is obtained.
4. Key parameters affecting ozone fumigation using forced-air circulation technique is determined in order to scale up to industrial level.

1.4 Keywords

Ozone, Dried chili, Degradation kinetics, Pesticide residue, Half-life period, Forced-air circulation

CHAPTER 2
LITERATURE REVIEW

2.1 General information of chili

Chili is a general agricultural crop which is commonly growth in all parts of the world. It belongs to family Solanaceae, as same as potatoes, tomatoes and egg plants. Capsicum annum or C. Frutescens is botanical name of chili. There are about 25 varieties of chili that are regularly grown all over the world. The plant of chili is typically a bushy of 60-80 cm in height. Plantation of chili needs humid and warm environment for growing. It is semi-perennials also grown as annual in cultivation (Hussain and Abid, 2011).

Chili is one of the most important vegetable industrial crop of Thailand. Chili can be planted in various types of soil. Northeast area of Thailand is a major area for the production of chili. Thai people consume a large amount of chili as indispensable condiment of every Thai household. Chili is daily consumed as common diets as either single ingredient or other food supplements. The Ministry of Public Health reported Thai's chili consumption of approximately 5 grams per day or 1 teaspoon (Ooraikul et al., 2011). Not only the chili consumption is for domestic market, but also the production of chili and its products are for exported to other countries. Thailand, India, China, Pakistan and Peru are among the largest chili producers and dried chili exporters in the world (Bhutia et al., 2015). In 2014 Thailand exported chili with the commercial quantity of 15,449 tons. The world demand is expectedly increasing, therefore it is predicted that there is a vast scope for exporting of chili.

Dried chili (Figure 1) is produced from fresh chili by removing of water using various technique such as sun drying, oven drying and freeze drying. The main objective of chili drying process is to extend shelf-life and reduce transportation cost. According to world production in 2006, approximately 25.9 million tons of fresh chili and 2.8 million tons of dried chili were produced. In Thailand, 420,000 tons of fresh chili was produced from 72,000 hectares of chili agricultural area with an approximate value of US$136 million (Montri et al., 2009).

Figure 1 General appearance of commercial dried chili.

2.1.1 Background of chili

Chili is originated from the Latin American tropical regions of the South (New Mexico and Guatemala) approximately 7500BC. The Mexico is considered the native home of Chilies. Prior to 1585 Portuguese brought hot chilies from Brazil to Indo-Pak subcontinent. Chili plays very important role in commercial sector. It is used in pharmaceutical industries, cosmetics, preparation of oleoresin and other industrial resources. There are many nutritionals, medicinal and economic benefits of its production. Chili is not only an important ingredient in food, but it is also used for culinary applications. It is used in foods for pungency and red color while it also contributes in part to the flavor. It contains numerous chemicals including steam-volatile oils, fatty oils, capsaicinoids, carotenoids, vitamins, protein, fiber and mineral elements (Bosland et al., 2012). It is also excellent source of Vitamins A, B, C, E and P. Fresh green chili peppers contain more vitamin C (340 mg per 100 gram) than citrus fruits and fresh red chili has more vitamin A than carrots. It is also used in food industry as chili paste, curry powder and other resources of food and bakers (Marín et al., 2004).

2.1.2 Dried chili

Dry chili peppers can be stored for months without deterioration. They are lighter in weight during transportation and their price is more stable. These chili peppers can be dehydrated by sun drying, with a water reduction of 80% in drying chambers to obtain seeds or in ovens

In 2010, the fresh chili pepper production from 68 countries was approximately 28,405.27 million tons, with China of 54%, followed by Mexico of 6.5%. The global production of dry chili peppers is 3,071 million tons, with production in India of 32%, China of 11%, Bangladesh and Peru of 7%. Mexico occupies the 10th place, with 60,000 tons in 37,000 Ha, representing the 2.6% of the global production. Mexico is the primary exporter of fresh green chili pepper and the sixth for dry chili pepper. Between 2000 and 2009, the average consumption per inhabitant was 15 kg of chili peppers per year (Rosas-Contreras et al., 2016; Tunde-Akintunde et al., 2005).

2.1.3 Pesticides in chili

Pesticides are essential in agriculture during a crop's growth, storage, and transport to control plant pests and diseases. To control pests, Thai farmers normally use excessive amount of chemicals and pesticides to protect their harvest and to increase productivity. To ensure sufficient pest control products, imported pesticides have been dramatically increasing from last decade. Because Thailand is located in tropical region, the climate does not only support agricultural activities, but also it supports livings of insect and other crop pests. As a result, the fields inhabitant significant populations of insects and pests during growing season (Taneepanichskul et al., 2014). Thailand is known as an agricultural country with more than 54.2% of its total area dedicated to agricultural production. It is reported that over half of the agricultural area (54.4%) is cultivated using pesticides, of which 45.9% is chemical contaminated. The majority of agricultural areas using pesticides are in the central and northeastern regions, which is account for 76.5% and 44.9%, respectively (Ooraikul et al., 2011). During mid March 2016, Thai Pesticide Alert Network (2017) (THAIPAN, 2017) randomly investigated pesticide residues in vegetables samples from various stores located in Bangkok, Chiang Mai and Ubon Ratchathani. The popular vegetables, including chili, basil, yard long bean, Chinese broccoli, Chinese cabbage, Chinese convolvulus, tomato, cucumber, Thai eggplant and cabbage, were sampled. The samples were obtained from 2 types of market as department store and supermarket that sale both non-certified and certified vegetables from National Bureau of Agricultural Commodity and Food Standards and Organic Thailand (THAIPAN, 2017) local market that sales local vegetables. The sampling method was carried out according to Codex procedure. Pesticide residues of 138 samples were investigated using Multi Residue Pesticide Screen (MRPS) method which covering 450 pesticides detection. This analysis was done by SAL laboratory in England that certified ISO/IEC17025:2005 by United Kingdom Accreditation Service (UKAS). The results were compared to Maximum Residue Limit (MRL) value according to Ministry of Public Health official announcement. The results showed that 100% of chili had the amount of pesticide residues exceeding limitation of MRL, as shown in Figure 2 (THAIPAN, 2017).

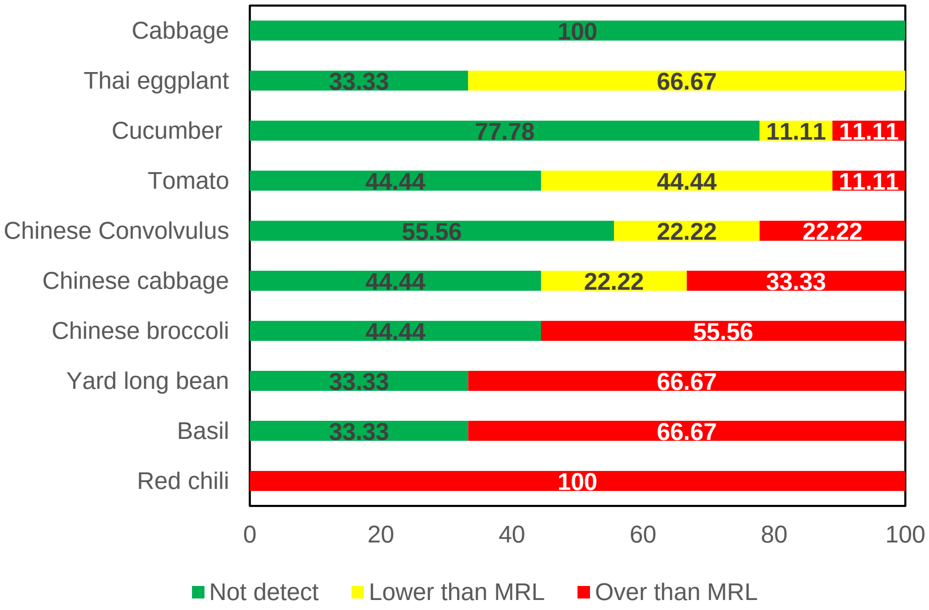


Figure 2 Pesticide residues in popular vegetable sampled by Thai Pesticide Alert Network.

Source: THAIPAN (2017)

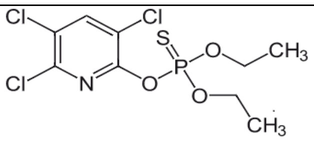
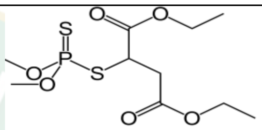
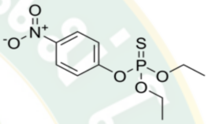
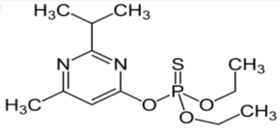
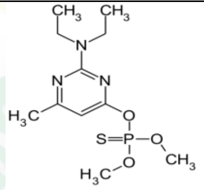
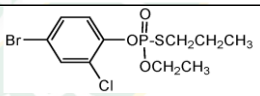
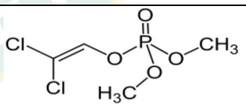
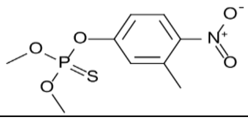
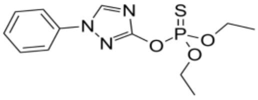
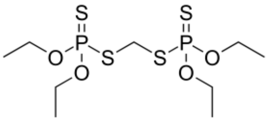
2.2 Background of pesticides

The widespread use of pesticides in public health and agricultural programs has caused severe environmental pollution and health hazards, including cases of severe acute and chronic human poisoning. An introduction of new, more toxic and rapidly disseminating pesticides into the environment has necessitated accurate identification of their potential hazards to human health. These toxic chemicals have become an integral part of the ecosystem, although many of them are extremely toxic to mammals and other non-target creatures. However, the implications of pesticide residues for human health have yet to be comprehensively documented. Free radicals play an important role in the toxicity of pesticides and environmental chemicals. Pesticides may induce oxidative stress, leading to generation of free radicals and alteration in antioxidants, oxygen free radicals, the scavenging enzyme system, and lipid peroxidation. The term "pesticides" is a general name that includes many chemicals, mostly in the classes of insecticides, namely organophosphates (OPs), organochlorines, carbamates and pyrethroids (Abdollahi et al., 2004).

2.2.1 Organophosphates pesticides

Organophosphates (OPs) are cholinesterase-inhibiting chemicals used predominately as pesticides. They are also used as chemical warfare agents (nerve agents). OPs include all insecticides containing phosphorous derived from phosphoric acid, and are generally the most toxic of all pesticides to vertebrate animals. OPs and carbamates inhibit the function of carboxylic ester hydrolases, such as the following substances (Abdollahi et al., 2004). Chymotrypsin, acetylcholinesterase (AChE), plasma or butyrilcholinesterase (BuChE), plasma and hepatic carboxylesterases (aliesterases), paraoxonases (asterases), and other nonspecific esterases within the body. The most prominent clinical effects of poisoning with OPs result from their inhibition of AChE. Several studies have demonstrated oxidative stress induced by OPs in rats and humans. Lipid peroxidation is also evident in rat brains and human erythrocytes. OPs-induced seizures have been reported, associated with oxidative stress (Sargazi et al., 2016). It has also been shown that the acute tubular necrosis which accompanies OPs toxicity is related to reactive oxygen species and lipid peroxidation (Abdollahi et al., 2004). The common organophosphates and chemical structure are shown in Table 1:

Table 1 The common organophosphates pesticides and their chemical structure.

Name	Chemical Structure
Chlorpyrifos	
Malathion	
Parathion	
Diazinon	
Pirimifos- methyl	
Profenofos	
Dichlorvos	
Fenitrothion	
Triazophos	
Ethion	

Source: Kazemi et al., 2012

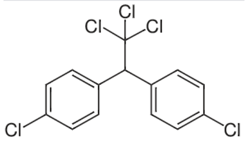
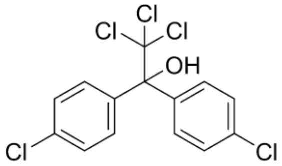
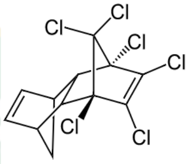
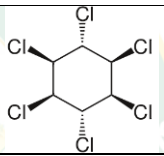
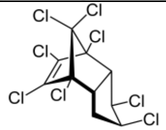
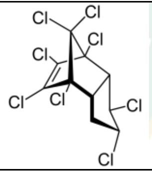
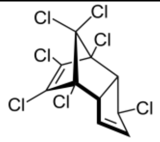
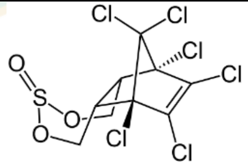
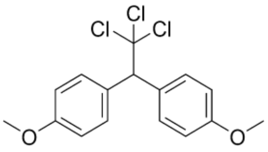
Organophosphates is toxic to living organs of human, insect and animals, including mammals, amphibians, and birds. The toxicity of organophosphate causes by phosphorylation of the acetylcholinesterase enzyme (AChE) at nerve endings. This leads to a damage of existing AchE. Therefore, the infected organ turns out to be overstimulated by the additional acetylcholine (ACh) in the nerve ending which is the impulse-transmitting chemical element. The enzyme is hazardous to ordinary control the transmission of nerve impulse from nerve fibers to smooth and skeletal muscle cells, autonomic ganglia and secretory cells, and inside the central nervous system (CNS).

2.2.2 Organochlorines pesticides

The organochlorines are insecticides that contain carbon, chlorine and hydrogen. They are also referred to as chlorinated hydrocarbons, chlorinated insecticides and chlorinated synthetics. The organochlorine insecticides may be divided into four distinct groups, including the following substances: 1) DDT (dichlorodiphenyltrichloroethane) and related analogs (methoxychlor), 2) cyclodienes (aldrin, endrin, heptachlor, dieldrin, chlordane, endosulfan, chlordecone), 3) hexachlorocyclohexane (lindane) and 4) related compounds (Abdollahi et al., 2004).

Since organochlorines are lipid solubles, these compounds are stored in fatty tissues, and repeated small exposures may result in accumulation and eventual clinical toxicity. Although all organochlorine insecticides are CNS stimulants, their exact mechanisms of action may vary. DDT and related compounds share a mechanism of action similar to the pyrethroids, whereas the cyclodienes, hexachlorocyclohexanes, toxaphene and related compounds are thought to exert their toxic effects through inhibition of gamma-aminobutyric acid. Organochlorine pesticides such as dieldrin, hexachlorobenzene (HCB) and dichlorodiphenyltrichlorethane (DDT). were banded and not available in the market several years ago due to its long half-life that could remain in the environment and food chain of human (Abdollahi et al., 2004).

Table 2 The common Organochlorines pesticides and their chemical structure

Name	Chemical Structure
Dichlorodiphenyltrichloroethane (DDT)	
Dicofol	
Eldrin	
Lindane	
cis-chlordane α-chlordane)	
trans-chlordane (γ-chlordane, beta-chlordane)	
Heptaclor	
Endosufan	
Methoxychlor	

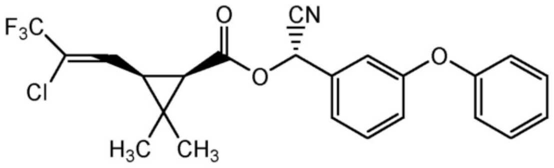
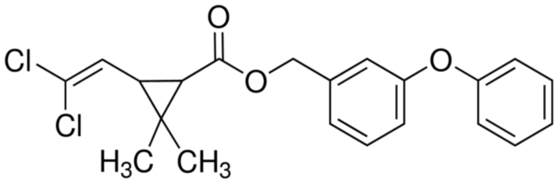
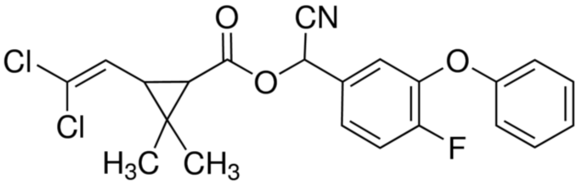
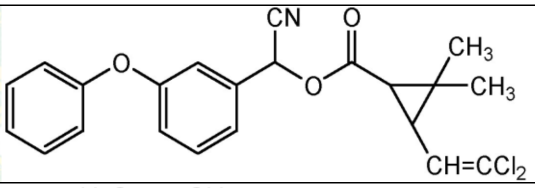
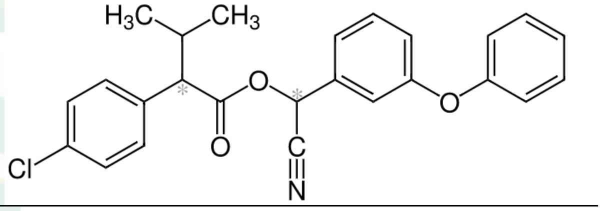
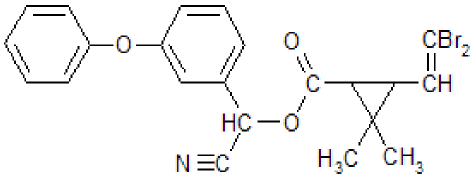
Source: Jararaj et al., (2016)

2.2.3 Pyrethrin and pyrethroid pesticides

Pyrethrins are natural insecticides, derived from yellow Chrysanthemum cinerariifolium and Tanacetum cinerariifolium, are among the oldest known insecticides that was first used in the 1800s. In addition, numerous synthetic derivatives known as pyrethroids have been produced, with greater chemical stability than the natural pyrethrins (Abdollahi et al., 2004).

Pyrethrin and pyrethroid aerosols are frequently used as automated insect sprays in public areas. Pyrethroid pesticides show high toxicity to a wide range of insects and low toxicity to mammals and birds, and rapid biodegradability. However, the liberal use of pyrethroids has increased the risk of intoxication for non-target species, such as birds, animals and organisms present in soil and water. Pyrethroids exert their insecticide effects through delaying closure of the inward sodium channel of the nerve membrane. Several studies have indicated that pyrethroids induce oxidative stress. Traces of this are evident in several organs, tissues, and cells, such as liver, brain, kidney and erythrocytes. The increase content of antioxidant enzymes, such as superoxide dismutase and catalase, which decomposes H_2O_2, and glutathione (GSH) in erythrocytes is probably an initial adaptive response to increased oxidative stress in pyrethroid intoxicated rats (Abdollahi et al., 2004).

Table 3 The common Pyrethroids pesticides and their chemical structure

Name	Chemical Structure
Cyhalothrin	
Permethrin	
Cyfluthrin	
Cypermethrin	
Fenvarelate	
Deltamethrin	

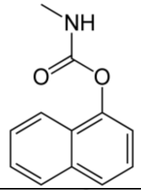
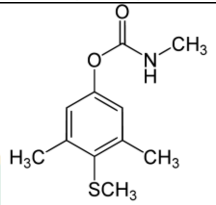
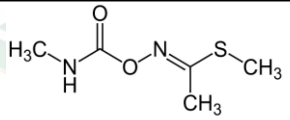
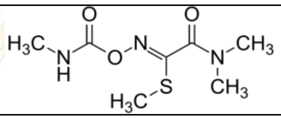
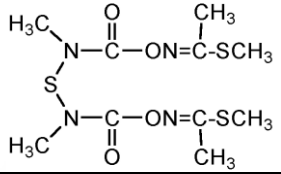
Source: Bradberry et al., (2005)

Pyrethrum is dermal and respiratory allergen, probably due mainly to noninsecticidal ingredients. Contact dermatitis and allergic respiratory reactions. Symptoms of poisoning in humans caused by pyrethroids are the effects on the nervous system and the severity of the symptoms depend on the type and amount of pyrethroids that retain in the body. Generally, no symptoms of pyrethroids were observed in at low dose. Acute poisoning caused by high doses of pyrethroids include dizziness, headache, vomiting, tingling, unconsciousness, death. Other symptoms of poisoning include skin irritation, itching, and redness. If eye contact may cause irritation. In addition, the toxicity of pyrethroids may depend on solvents and in liquid doses. It may cause breathing into the lungs and may lead to chemical pneumonitis. While limited absorption may account for the low toxicity of some pyrethroids, rapid degradation by mammalian liver enzymes is probably the key factor responsible for the phenomenon. The LD50 for weanling rats with deltamethrin has been reported at 12 mg.kg^{-1}, while the adult LD50 is about 80 mg.kg^{-1}.

2.2.4 Carbamate pesticides

Carbamate pesticides are derived from carbamic acid and kill insects in a similar fashion as organophosphate insecticides. They are widely used in homes, gardens, and agriculture. Like the organophosphates, their mode of action is an inhibition of cholinesterase enzymes, affecting nerve impulse transmission. The first carbamate, carbaryl, was introduced in 1956, and more of it has been used throughout the world than all other carbamates combined. Because of carbaryl's relatively low mammalian oral and dermal toxicity and broad control spectrum, it has had wide use in lawn and garden settings. Most of the carbamates are extremely toxic to Hymenoptera, and precautions must be taken to avoid exposure to foraging bees or parasitic wasps. Some of the carbamates are translocated within plants, making them an effective systemic treatment (Fishel, 2005).

Table 4 The common carbamate pesticides and their chemical structure

Name	Chemical Structure
Carbaryl	
Methiocarb	
Methomyl	
Oxamyl	
Thiodicarb	

Source: Gupta (2011)

Carbamates are N-methyl Carbamates derived from a carbamic acid and cause carbamylation of acetylcholinesterase at neuronal synapses and neuromuscular junctions. While they possess a similar mechanism of action to the irreversible phosphorylation of acetylcholinesterase by organophosphates, carbamates bind to acetylcholinesterase reversibly. Consequently, carbamates have a comparable toxicological presentation to organophosphate poisonings with a period of toxicity that is usually less than 24 hours.

2.3 Background of ozone

Nowadays, increasing attention is focusing on food safety and develop intervention methods to reduce and/or eliminate human pathogens from consumer’s products. Traditional technology utilizes water with/without sanitizing agent to wash fresh food and cleanup the product. Many research and industrial trials are underway to validate the use of ozone in the food industry as an alternative treatment to improve food safety. Ozone is a strong oxidant and potent disinfectant agent. Notably, when ozone is applied to food surface, it leaves no residues since it decomposes quickly. Numerous ozone applications have been installed throughout the food industry around the world during the past ten years. Chemical and physical properties of ozone, its generation, and antimicrobial power of ozone were explained as well as many advantages of ozone use in the food industry (Gonçalves, 2009; Gonçalves and Gagnon, 2011).

2.3.1 General information of ozone

Ozone is a strong oxidant and one the most powerful antimicrobial substance (natural sanitizing and disinfecting agent) in the world destroying up to 99.9% of pesticides and microorganisms commonly found on food due to its potential oxidizing capacity. Any pathogen or contaminant can be disinfected, altered or removed via an oxidation process of ozone. It is the strongest of all molecules available for disinfection in water treatment, and is second only to elemental fluorine in oxidizing power.

Usage of ozone may have many advantages in the food industry. There are suggested applications of ozone in the food industry such as food surface hygiene, sanitation of food plant equipment, reuse of wastewater, lowering biological oxygen demand (BOD) and chemical oxygen demand (COD) of food plant waste.

In the United States, ozone has received in 1997 GRAS (Generally Recognized as Safe) classification, and in 2001 the FDA officially approved media containing ozone for use in the food industry, also for direct contact with food products, including fish, meat and poultry. Multi-functionality of ozone application makes it as a promising agent (Gonçalves, 2009; Gonçalves and Gagnon, 2011).

2.3.2 History of ozone

Ozone has being used continuously for years to disinfect water for drinking purposes in Europe, beginning in Nice (France), in 1906 and thereafter at water treatment plants throughout the world. A number of other commercial uses have been found for ozone including disinfection of bottled water, swimming pools, prevention of fouling of cooling towers, and wastewater treatment. Ozone was first used in the United States in 1908, with minimal growth until 1985. In 1980 there were less than 10 known operating ozone treatment plants. However, within the past two decades more than 300 ozone treatment plants have been designed, constructed and operated to address disinfection, disinfection by-products (DBP's), taste and odor, color, micro-coagulation (micro-flocculation), hydrogen sulfide, and other drinking water treatment needs. Since the 1920's scientists have tried to take advantage of long-range disinfection characteristics from ozone, as to slow down the decomposition, as it improves the security of fishing products. The recent advances in electronics and technology of ozone have allowed the development of new line of compact ozone generators. The brief history of ozone use for water and food products is listed below.

The recent expert panel recommendation to the FDA supporting GRAS classification of ozone as a disinfectant for foods has opened the door for the produce industry to establish independent affirmation of safety when applied in a manner consistent with good manufacturing practices. When using ozone for produce contact, a copy of the public disclosure of the expert panel must be available on-site for an inspector requesting the authority upon which GRAS classification is presumed (Gonçalves, 2009; Gonçalves and Gagnon, 2011).

2.3.3 Properties and structure of ozone

Ozone (O_3) is an allotropic form of oxygen (O_2), i.e., it is made up of same atoms, but they are combined in different form. The difference is the presence of three oxygen atoms, whereas common oxygen has only two atoms. It has low molecular weight (MW = 48) whose three oxygen atoms chemically are arranged in chain. Ozone is then enriched oxygen (O_3). Ozone is one of the oxidants more powerful than they are known, and for this reason it has a strong capacity of disinfection and sterilization. Their disinfectants properties are superior to those of oxygen. It is a powerful germicide which destroys all class of bacteria and fungi, not allowing their development. The high chemical reactivity of ozone is related to its stable electronic configuration which impels to look for electrons from other molecules. During the reaction with other molecules, ozone is destroyed. The final products of organic molecule oxidation with ozone are carbon dioxide and the water. Unlike other biocides agents such as chlorine, the time necessary to make the disinfection is lower. For this reason, it' s very effective in destruction of chlorine resistant microorganisms due to a power of reaction of three thousand times superior to the chlorine, which turns it is a possible biocide agent, as much for the water treatment, like for the treatment of air and closed atmospheres (Gonçalves, 2009; Gonçalves and Gagnon, 2011).

Table 5 Oxidizing potential of various reagent

Oxidant agent	Oxidizing Potential (mV)	Reactive power of oxidation
Fluorine	3.06	2.25
Ozone	2.07	1.52
Hydrogen Peroxide	1.77	1.30
Hypochlorous acid	1.49	1.10
Chlorine gas	1.36	1.00

Source: Gonçalves (2009)

Table 6 Comparison of physical and chemical properties between ozone and oxygen.

Property	Ozone	Oxygen
Molecular Formula	O_3	O_2
Molecular weight	48 g.mol^{-1}	32 g.mol^{-1}
Color	Light blue	colorless
Smell	Clothes after being outside on clothesline Photocopy machines, smell after lightning storms	odorless
Boiling Point	-111.3°C	-183°C
Density	2.141 kg.m^{-3}	1.429 kg.m^{-3}
Solubility in water (LO_3/LH_2O)	0.64 (190 mgL^{-1})	0.049 (14.6 mgL^{-1})

Source: Gonçalves (2009)

Ozone has strong oxidizing potential as shown in Table 5. It is very appropriate for the water treatment with high organic content. About this form, an ozone treatment in organic wastes can be considered an effective and faster form, that other treatments with chlorine or hydrogenperoxide. In addition, the treatment with ozone is not exclusive and can be combined with the use of hydrogen peroxide or ultraviolet radiation, which results in a synergic effect. Another property of ozone is the capacity of absorption of flavors and strange smells in the water. This must simply to the fast destruction of organic compounds responsible for the smell. In the same way, ozone has a deodorization role of the air. In waters also, it is useful for the elimination from heavy metals like iron and manganese that precipitate quickly in oxide form. In normal conditions of pressure and temperature, ozone is unstable. This instability increases with the temperature and the humidity, arriving to be total over 200°C. On the contrary, its greater degree of stability reaches to – 50°C and 38 mm Hg of pressure, in other words, a twentieth part of the atmospheric pressure. At room temperature, ozone attacks saturated organic compounds slowly. This offensive capability increases at temperatures of and even inferior 78°C. Ozone has a longer half-life in the gaseous state than in aqueous solution (Table 7). Ozone in pure water rather quickly degrades to oxygen, and even more rapidly in impure solutions. Ozone solubility in water is 13 times that of oxygen at 0–30°C and it is progressively more soluble in colder water. Ozone decomposition is faster at higher water temperatures (Gonçalves, 2009; Gonçalves and Gagnon, 2011).

Table 7 Typical O_3 half-life vs. temperature between gaseous and aqueous states.

Gaseous		Aqueous (pH7)	
Temp (°C)	**Half-life***	**Temp (°C)**	**Half-life***
-50	3 months	15	30 minutes
-35	18 days	20	20 minutes
-25	8 days	25	15 minutes
20	3 days	30	12 minutes
120	1.5 hours	35	8 minutes
250	1.5 sec	-	-

* These values are based on thermal decomposition only. No wall effects, humidity, organic loading, or other catalytic effects are considered.

Source: Gonçalves (2009)

The solubility of ozone (Table 8) depends on the water temperature and the ozone concentration in the gas phase. The properties of greater interest of ozone are their solubility in water and its liquid and in the middle gaseous stability, since they are those that allow taking ahead their application like disinfectant. The final ozone concentration in the water is function of the concentration in phase gas, the pressure of the gas and the temperature of the water and the technology of interchange liquid/gas. It depends on the technology used in the generation and the carrying gas such as air or oxygen (Gonçalves, 2009; Gonçalves and Gagnon, 2011).

Table 8 Ozone Solubility at different temperatures.

Temp (°C)	Solubility (LO_3/LH_2O)
0	0.640
15	0.456
27	0.270
40	0.112
60	0

Source: Gonçalves (2009).

2.3.4 Mechanisms of oxidations

Ozone have reaction by direct or indirect oxidation by ozonolysis, and by catalysis. The three major action pathways occur as follows

- Direct oxidation reactions of ozone resulting from the action of an atom of oxygen, are typical first order, high redox potential reactions.
- In indirect oxidation reactions of ozone, the ozone molecule decomposes to form free radicals (OR) which react quickly to oxidize organic and inorganic compounds.
- Ozone may also act by ozonolisys by fixing the complete molecule on double linked atoms, producing two simple molecules with differing properties and molecular characteristics. Ozone destroys microorganisms by the progressive oxidation of vital cellular components. Ozone oxides polyunsaturated fatty acid sorsulphydryl and amino acids of enzymes, peptides and proteins to shorter peptides. Ozone degradation of the cell envelope unsaturated lipids result in cell disruption and subsequent leakage of cellular contents. In Gram-negative bacteria, the lipoprotein and lip polysaccharide layers are the sites of destruction, resulting in increases in cell permeability and eventually cell lyses. Cellular death can also occur due to the potent destruction and damage of nucleic acids (Gonçalves, 2009; Gonçalves and Gagnon, 2011).

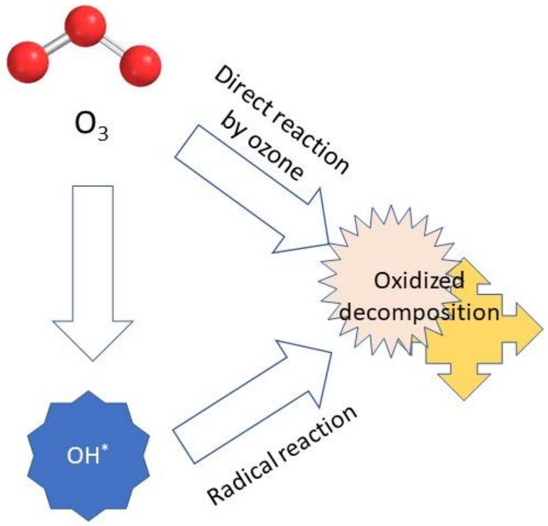


Figure 3 Scheme of ozone oxidation

Source: Jiménez et al. (2019)

2.3.5 Byproducts of ozone

In oxidation reactions of ozone with organic substance, at least one by-product would be obtained as a simple chemical structure in each stage of oxidation. If oxidation is occured in adequate amount and for enough time period, a large number of organic materials could be completely oxidized to carbon dioxide and water as final products. The completed oxidation is infrequent, especially in most industrial cases, in which the treatment propose usually is to eliminate or reduce some offensive parameter (color, odor, organic matters, some particular contaminant, or a specific microorganism). Therefore, lots of by-product from the oxidation process can be produced during ozonation or ozone advanced oxidation process (Llusia et al., 2002; Ma and Graham, 2000).

Normally, the organic by-product occurred by oxidation of ozone consists of various kinds of organic substances such as acids, alcohol, ketone, aldehyde, and mixed functionality derivatives (aldehydes–alcohol, keto-acides, keto–aldehyde, aldehyde – acids, etc.) which are much more easily biodegradable than are the staring compounds prior to ozone oxidation. In the water treatment plant and treated water, these types of compounds are sent to distribution system without a residual of chlorine, considerable regrowth of microorganisms (feeding on ozone – oxidized organic by – product) can occur. To make sure the inhibition of this regrowth, biological filtration step after ozonation in the water treatment process is required in most water treatment plants employing ozone provide. This process is provided prior to adding a small residual of chlorine or chloramine using a granular activated carbon as the filter medium, after development of the appropriate biomass on the Granular – Activated Carbon (GAC) surface, the ozone – product organic by products can be mineralized (converted biochemically to carbon dioxide and water) in a short time. Any inorganic material that could be oxidized by ozone will be converted into its highest valence state. Ferrous iron is transform quickly to ferric ion, which in water, rapidly hydrolyzed to generate ferric hydroxide. Cyanide anion is oxidized rapidly by ozone to cyanate anion, which slowly hydrolyzes to generate carbon oxides and nitrogen gas. Nitrite anion rapidly produces nitrate anion upon ozonation. Sulfide ions first forms elemental sulfur, but continued ozonation produces sulfite, sometimes sulfur trioxide, and ultimately sulfate anion. Manganous ion rapidly oxidizes to form the insoluble manganese dioxide. However, continuous ozonation can convert this into the soluble permanganate anion. Ozone oxidation of bromide ion in water is chemically complex and can lead to the formation of brominated organics as well as bromate anion. The first step in the oxidation of bromide ion (by ozone or chlorine) is the formation of hypobromous acid/hypobromite ion (so – called – free bromide II). Hypobromous acid, in turn, is as outstanding brominating chemical substance. Moreover, it is the source of mixed bromo-chlor-organics when chlorine is mixed into waters comprising natural organics. Ozonation of hypobromite ion can produce bromate anion (Llusia et al., 2002; Ma and Graham, 2000).

2.3.6 Advantages and disadvantages of ozone

Ozone technology has several significant advantages over its chemical alternatives as follows (Gonçalves, 2009; Gonçalves and Gagnon, 2011):

1) Ozone can be generated on-site.

2) Ozone is one of the most active, readily available oxidizing agents.

3) Ozone rapidly decomposes to oxygen leaving no traces.

4) Reactions do not produce toxic halogenated compounds.

5) Ozone acts more rapidly and more completely than other common disinfecting agents do.

6) Ozone reacts swiftly and effectively on all strains of viruses.

For ozone disadvantages, it could be shown as follows (Gonçalves, 2009; Gonçalves and Gagnon, 2011):

1) High capital cost compared with other oxidation/disinfection chemical reagent.

2) Since ozone is the most powerful oxidizing agent available, it is also potentially the most dangerous of oxidants. This danger was recognized in the early stages of ozone research and techniques have been developed to insure the absence of ozone accidents.

3) While ozone is a potent oxidant and can reduce bacterial levels in pure culture, the use in food processing operations where bacteria exist within organic material is more difficult.

2.3.7 Ozone generation

The ozone production takes place generally by the ventilation of electrical discharges of high voltage in the air or pure oxygen. This radiation affects a common oxygen molecule that is found in atmosphere which produces the split of the molecule and separation of free oxygen atom. These atoms collide with other oxygen molecules, forming therefore ozone molecules. The energy absorbed by an oxygen molecule break it in two oxygen atoms (Gonçalves, 2009; Gonçalves and Gagnon, 2011).

$$O_2 + hv \rightarrow O + O$$

1) Each one of these atoms is joined to an oxygen molecule to give another one of ozone.

$$O + O_2 \rightarrow O_3$$

2) Finally, the ozone molecule is destroyed again absorbing more ultraviolet radiation.

$$O_3 + hv \rightarrow O + O_2$$

3) Ultraviolet energy is absorbed in a closed cycle of formation and destruction of the ozone

In order to generate ozone, a diatomic oxygen molecule must first be split. The resulting free radical oxygen is thereby free to react with other diatomic oxygen to form the triatomic ozone molecule. However, in order to break the O–O bond, a great deal of energy is required. Ultraviolet radiation (188nm wave length) and corona discharge methods can be used to initiate free radical oxygen formation and, thereby generate ozone. In order to generate commercial levels of ozone the corona discharge method is usually used (Gonçalves, 2009; Gonçalves and Gagnon, 2011).

2.3.7.1 Corona discharge

There are two electrodes in corona discharge, one of which is the high tension electrode and the other is the low tension electrode (ground electrode). These are separated by a ceramic dielectric medium and narrow discharge gap is provided (Figure 1). When the electrons have sufficient kinetic energy (around 6–7 eV) to dissociate the oxygen molecule, a certain fraction of these collisions occur and a molecule of ozone can be formed from each oxygen atom. In synthesis, electrical energy flowing across a narrow gap that is filled with oxygen splits the oxygen molecules into oxygen atoms (O). These atoms combine with other oxygen molecules (O_2) to form ozone (O_3), as illustrated in Figure 4. The unstable ozone gas quickly reverts back to molecular oxygen; thus, it cannot be stored in a container. If air is passed through the generator as a feed gas, a 1-4% of ozone can be produced. However, use of pure oxygen allows yields to reach to 16% ozone. Consequently, ozone concentration cannot be increased beyond the point that the rates of formation and destruction are equal. Ozone gas cannot be stored since ozone spontaneously degrades back to oxygen atoms. The advantage of Corona Discharge are: high ozone concentrations; best for water applications; fast organic (odor) removal; equipment can last for years without maintenance. (Gonçalves, 2009; Gonçalves and Gagnon, 2011).

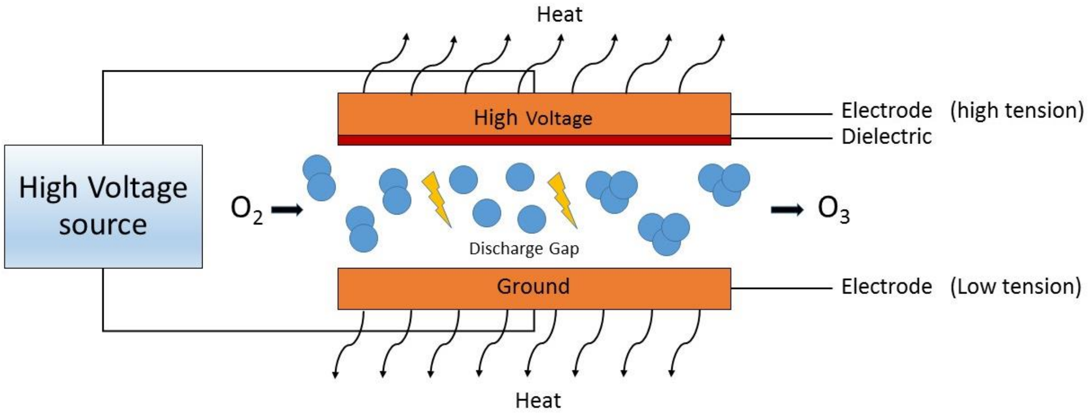


Figure 4 Scheme of corona discharge method

Source: Gonçalves (2009)

2.3.7.2 Ultraviolet radiation

The method is based on conversion of oxygen on ozone molecules by lam of ultraviolet light (wavelength of 188 nm, Figure 5). Nevertheless, the ozone production is of low intensity. At low temperatures, the process of ozone ventilation is made with greater facility. The ozone formed, after certain period of time, is degraded spontaneously in oxygen. The advantages of UV light are: simple construction; lower cost than corona discharge; output hardly affected by humidity; fewer by-products compared to corona discharge (Gonçalves, 2009; Gonçalves and Gagnon, 2011).

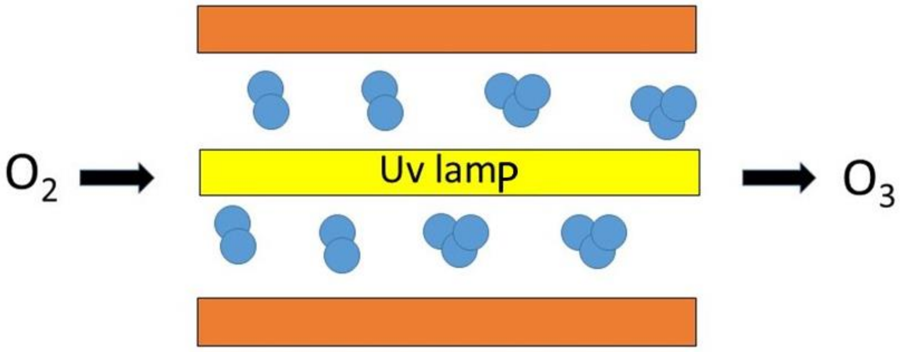


Figure 5 Scheme of ultraviolet radiation method

Source: Gonçalves (2009)

2.3.7.3 Electrolytic

The production of ozone by electrolytic process has historical prominence due to artificial ozone was first discovered from the electrolysis of sulfuric acid by Schonbein in 1840. This method is attractive for small – scale application especially in rural areas due to the uncomplicatedness of the apparatus and process. Numerous probable benefits of ozone are correlated with electrolytic generation, including, possible generation of ozone at high concentrations, reduced equipment size, no feed gas preparation, the use of low – voltage DC current and generation in the water, disregarding contacting processes of the ozone – to – water (Shiue et al., 2006).

2.3.7.4 Radiochemical

One of the methods for ozone generation is the utilization of radioactive rays to generate high energy irradiation. This process is interesting due to it could produce high yield of ozone by the promising thermodynamic and it can use waste fission isotopes as starting material. However, the process is too complicated to apply in real water treatment (Garcia, 1980; Obenshain, 1982).

2.3.8 Corrosion and degradation of materials

The power of ozone as an oxidant requires careful selection of construction material in design to provide a facility that is resistant to the attacks of gas-phase ozone. This provides general information on material compatibility with ozone. The performance depends on the environment (dry or moist air, water, concentration of ozone, whether the materials have been modified for ozone service, etc) and application (polycarbonateis stable in the presence of ozone but yellows over time which reduces its utility where clarity is important).

Table 9 Ozone compatibility with surfaces of material

Material	Compatibility	Material	Compatibility
304 stainless steel	B-Good	Kalrez	A- Excellent
316 stainless steel	A- Excellent	Kel-Fr	A- Excellent
ABS plastic	B-Good	LDPE	C-Fair
Acetal (Delrinr)	C-Fair	Natural rubber	D-Severe effect
Aluminum	B-Good	Neoprene	C-Fair
Bronze	B-Good	Nylon	D-Severe effect
Buna N (Nitrile)	D-Severe effect	Polycarbonate	A- Excellent
Carbon Steel	C-Fair	Polyetherether-Ketone(PEEK)	A- Excellent
ChemRaz (FFKM)	B-Good	Polypropylene	B-Good
Copper	A- Excellent	Polyurethane	A- Excellent
CPVC	A- Excellent	PTFE	A- Excellent
EPDM	A- Excellent	PVC	B-Good
Fluorocarbon(FKM)	A- Excellent	PVDF(Kynar®)	A- Excellent
Hypalonr	A- Excellent	Silicone	A- Excellent
Hytrelr	C-Fair	Viton	A- Excellent

Ratings = Chemical Effect

A = Excellent.

B = Good: Minor Effect, slight corrosion or discoloration.

C = Fair: Moderate Effect, not recommended for continuous use. Softening, loss of strength, swelling may occur.

D = Severe: Effect, not recommended for ANY use.

Source: Gonçalves (2009)

2.3.9 Residual ozone destruction

2.3.9.1 Thermal process

Oxygen can be produced by the degradation of ozone at high temperature. The process is simple by utilization of thermal ozone destroyer using vent gas heating. The advantages of this method are low cost of materials and instrument, convenient and easy to set up. However, it requires high power compared to other ozone destruction techniques. Therefore, the application of this method is usually used in small system. Basically, all of the gas that passes through the contact/reaction vessel must be heated to the decomposition temperature (gas from the ozone generator, water vapor from the reactor vessel and any that leaks into the contact tank)

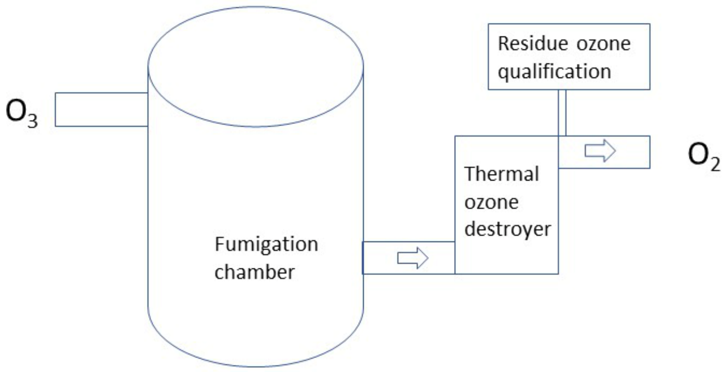


Figure 6 Thermal ozone destroyer

Source: de Oliveira et al. (2020)

2.3.9.2 Thermal catalytic

For the destruction of ozone by thermal catalytic process, catalyst will be used at high temperature to enhance ozone degradation activity. In addition, using of catalyst could reduce energy requirement for the ozone destruction process. The popular catalyst is manganese dioxide. By the way, cost of catalyst is higher than cost of energy reduction as compared to the thermal process.

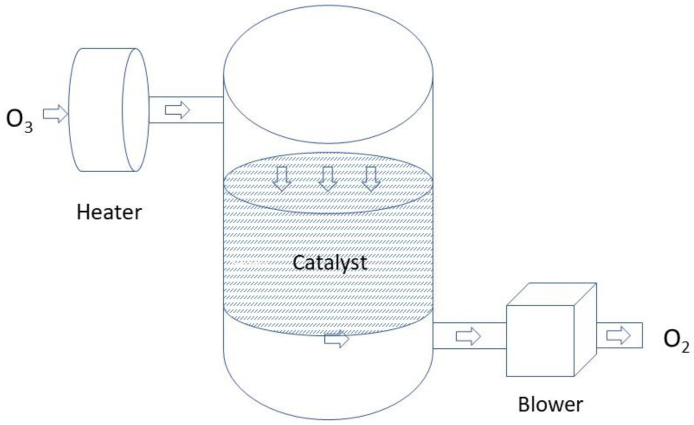


Figure 7 Thermal catalytic ozone destroyer

Source: Carus (2020)

2.3.9.3 Heat recovery systems

One more solution to decrease cost of thermal based ozone destruction technique is to apply heat discovery system by using treated vent gas to heat incoming vent gas. This recollect allocate if the energy expended to increase temperature of the vent gas and decrease total energy consumption. The heat recovery system are only applied in the large-scale ozone systems.

2.3.10 Food industry application

Ozone is a powerful antimicrobial substance due to its potential oxidizing capacity. Ozone use may have many advantages in the food industry. There are suggested applications of ozone in the food industry such as food surface hygiene, sanitation of food plant equipment, reuse of wastewater, lowering biological oxygen demand and (BOD) and chemical oxygen demand (COD) of food plant waste. Ozone has been shown to deactivate a large number of organisms, including bacteria, fungi, yeast, parasites and viruses, and can also oxidize natural organic compounds as well as synthetic substances, such as detergents, herbicides and composite pesticides. Ozone has been used in the food processing industry, both as gaseous ozone and dissolved in water to reduce bacteria on a wide range of food products and contact surfaces. The application of ozone in the food storage has been applied in freezing chambers and warehouses (meats, seafood, fruits, vegetables, cheeses, sausages, etc.). The main objective is to reduce the bacteriological index that occur in the mentioned storage systems, obtain greater durability of foods (in refrigeration, freezing or fresh storage) and eliminating bacteria to not allow to growth in meats or others, formation of moulds, etc (Gonçalves, 2009; Gonçalves and Gagnon, 2011).

2.4 Kinetic determination

Reaction kinetics is defined as the study of the rates of chemical reactions and their mechanisms. Reaction rate is simply defined as a change in a measurable quantity divided by the change in time. There are several types of kinetic reaction as follows:

- Zero-order reaction
- First-order reaction
- Second order reaction

2.4.1 Zero–order reactions

For a zero-order reaction, the integrated rate law shows a straight line corresponding to Equation (1).

$$[A] = [A]_0 - kt \qquad (1)$$

Where $[A]_0$ = initial concentration of pesticide A, at fumigation time = 0

$[A]$ = concentration of pesticide A, at fumigation time

t = fumigation time

Equation 1 has the form of the algebraic equation for a straight line, y = mx + b, with y = [A], mx = $-kt$, and b = $[A]_0$). The rate constant (k) of a zeroth-order reaction must have the same units as the reaction rate.

2.4.2 First-order reaction

For the first-order reaction, the reaction rate depends on the concentration of one of the reactants. The integrated rate law for a first-order reaction could be shown in two different equations, exponential equation and logarithm equation. The exponential equation is showed as Equation (2).

$$[A] = [A]_0\ e^{-kt} \qquad (2)$$

Where $[A]_0$ = The initial concentration of pesticide A, at fumigation time = 0

[A] = The concentration of pesticide A, at fumigation time

t = Fumigation time

k = The rate constant

e = The base of the natural logarithms = 2.718

The integrated rate law is corresponding to the relationship between fumigation time and pesticide concentration. Equation (2) shows that the concentration of A will decline in a smooth exponential curve over time. By taking the natural logarithm of each side of Equation (2) and rearranging, an alternative logarithmic expression of the relationship between the concentration of A and t will be obtained as shown in Equation (3).

$$\ln[A] = \ln[A]_0 - kt \qquad (3)$$

Since Equation (3) has the form of the algebraic equation for a straight line, $y = mx + b$, with $y = \ln[A]$ and $b = \ln[A]_0$, therefore a plot of ln[A] versus t for a first-order reaction should give a straight line with a slope of $-k$ and an intercept of $\ln[A]_0$.

2.4.3 Second-order reaction

For the reaction 2A→ products, the following integrated rate law describes the concentration of the reactant at a given time:

$$\frac{1}{[c]} = \frac{1}{[c]_0} + kt \qquad (4)$$

Since Equation (4) has the form of an algebraic equation for a straight line, $y = mx + b$, with $y = 1/[A]$ and $b = 1/[A]_0$, therefore a plot of $1/[A]$ versus t for a simple second-order reaction is a straight line with a slope of k and an intercept of $1/[A]$

2.5 Dimensional analysis

Although many practical engineering problems involving momentum, heat and mass transport can be demonstrated and solved using the equations and procedures described, as important number of them can be solved only by relating a mathematical model to experimentally obtained data.

In fact, it could be stated that very few problems involving real momentum, heat, and mass flow can be solved by mathematical analysis alone. The solution to many practical problems is achieved using a combination of theoretical analysis and experimental data. Thus engineers working on chemical and bio-chemical engineering problems should be familiar with the experimental method to these problem. They have to interpret and make use of the data obtained from others and have to be able to plan and execute the strictly necessary experiments in their own laboratories. Some techniques and Ideas which are important in the planning and execution of chemical and bio-chemical experimental research. The basic considerations of dimensional analysis and similitude theory are also used in order to help the engineer to understand and correlate the data that have been obtain by other researchers (Sonin, 2001).

One of the goals of experimental research is to analyze the systems in order to make them as widely applicable as possible. To achieve this, the concept of similar systems (e.g. industrial units). The laboratory systems are usually thought of as models and are used to study the phenomenon of interest under carefully controlled condition, empirical formulations can be developed, or specific predictions of one or more characteristics of some other similar system can be made from the study of these models. The establishment of systematic and well-defined relationships between the laboratory model and the “order” systems is necessary to succeed with this approach. The correlation of experimental data based on dimension analysis and similitude produces model described in the dimensional analysis. However, dimensional analysis and similitude do not have a theoretical basic (Sonin, 2001).

This research applies the procedure of dimensional analysis and describes Buckingham's π-theorem, which follow from 4 step. The premise of dimensional analysis is that the form of any physically significant equation must be such that the relationship between the actual physical quantities remains valid independent the magnitudes of the base unit. Dimensional analysis derives the logical consequences of this premise

Suppose we are interested in some particular physical quantity Q_0 that is a “dependent variable” in a well-defined physical process or event. By this we mean that, once all Q_0 the quantities that define the particular process or event are specified, the value of Q_0 follows uniquely (Sonin, 2001).

Step 1: The independent variables

The first and most important step in dimensional analysis is to identify a complete set of independent quantities $Q_0 ... Q_n$.that determine the value of Q_0

$$Q_0 = (\int Q_1, Q_2, ..., Q_n) \tag{5}$$

A set $Q_{1,}...Q_n$ is complete if, once the values of the members are specifies no other quantity can affect the value of Q_0 and independent if the value of each member can be adjusted arbitrarily without affection the value of any other member.

Starting with a correct set $Q_{1,}...Q_n$ is as important in dimensional analysis as it is in mathematical physics to start with the correct fundamental equation and boundary condition. If the starting point is wrong, so is the answer. The relationship expressed symbolically in Equation (5) is the result of the physical laws that govern the phenomenon of interest. It is our premise that its form must be such that, once the values $Q_{1,}...Q_n$ are specified, the equality holds regardless of the *sizes* of the follow derive the consequences of this premise (Sonin, 2001).

Step 2: Dimensional considerations

Next, the dimension is listed. The dependent variable Q_0 and the independent variables $Q_{1,}...Q_n$. As we have discussed, the dimension of a quantity depends on the *type* of system of unit and we must specify at least the type the system of unit before we do this. All quantities have dimension of the form

$$\left[Q_i\right] = L^{l_i} M^{m_i} t^{\tau_i} \tag{6}$$

Where the exponents l_i, m_i and t^{τ_i} are dimensionless numbers that follow form each quantity's definition

We now pick from the complete set of physically independent variables $Q_{1,}...Q_n$ a complete, dimensionally independent subset $Q_{1,}...Q_k$ $(k\leq n)$, and express the dependent variable Q_0 as a product of powers of$Q_{1,}...Q_k$. All physical quantities have dimensions which can be expressed as products of powers of the set of base dimension. Alternatively, it is possible to express the dimension of one quantities which are not necessarily base quantities. A subset $Q_{1,}...Q_k$ of the set $Q_{1,}...Q_n$ is dimensionally independent if none of its members has a dimension that can be expressed in terms of the dimensions of all the remaining quantities $Q_{k+1}...Q_n$ of the full set can be expressed in terms of the dimensions of the subset$Q_{1,}...Q_k$.

Since Equation (5) is dimensionally homogeneous, the dimension of the dependent variable Q_0 is also expressible in terms of the dimensions of$Q_{1,}...Q_k$.

The dimensionally independent subset $Q_{1,}...Q_k$ is picked by trial and error. Its members may be picked in different ways, but the number k of dimensionally independent quantities in the full set $Q_{1,}...Q_n$ is unique to the set, and cannot exceed the number of base dimensions which appear in the dimensions the quantities in that set. For example, if the dimension of $Q_{1,}...Q_n$ involve only length, mass and time then $k \leq 3$

Having chosen a complete, dimensionally independent subset$Q_{1,}...Q_k$, we express the dimension of Q_0 and the remaining quantities $Q_{k+1}...Q_n$in terms of the dimension of$Q_{1,}...Q_k$. These will have the form

$$\left[Q_i\right] = \left[Q_1^{Ni1} Q_2^{Ni2} .....Q_k^{Nik}\right] \tag{7}$$

If *i* > *k* or *i* = 0. The exponents N_{ij} are dimensionless real numbers and can om most cases be found quickly by inspection, although a formal algebraic method can be used.

The formal procedure can be illustrated with an example where length, mass and time are the only base quantities, in which case all dimensions have the form of equation (6). Let us take Q_1, Q_2 and Q_3 as the complete dimensionally independent subset. Equating the dimension given by equation (6) with that of equation (7), we obtain three equations (Sonin, 2001).

$$l_i = \sum_{j=1}^{3} N_{ij} l_j$$

$$m_i = \sum_{j=1}^{3} N_{ij} m_j \tag{8}$$

$$t_i = \sum_{j=1}^{3} N_{ij} t_j$$

Which can be solved for the three unknowns N_{i1}, N_{i2} and N_{i3}

Step 3: Dimensionless variables

The *dimensionless forms* of the n-k is defined, remaining independent variable by dividing each one with the product of power of $Q_{1,}...Q_k$ which has the same dimension,

$$\pi_i = \frac{Q_{k+i}}{Q_1^{N(k+i)1} Q_2^{N(k+i)2} Q_k^{N(k+i)k}} \qquad (9)$$

Where I = 1, 2,..., n-k and a dimensionless form of the dependent variable Q_0

$$\pi_0 = \frac{Q_0}{Q_1^{N_{01}} Q_2^{N_{02}} Q_k^{N_{03}}} \qquad (10)$$

Step 4: The end game and Buckingkam's π-theorem

An alternative form of equation (10) is

$$\pi = \int (Q_1, Q_2, ...Q_k; \pi_1.\pi_2, ...\pi_{n-k}) \qquad (11)$$

In which all quantities are dimensionless except $Q_{1,}...Q_k$. The values of the dimensionless quantities are independent of size of the base units. The value of $Q_{1,}...Q_k$, on the other hand, do depend on base unit size. They cannot be put into dimensionless form since they are (by definition) dimensionally independent of each other. From the principle that any physically meaningful equation must be dimensionally homogeneous, that is, valid independent of the size of the base unit, it follow that $Q_{1,}...Q_k$ must in fact be absent form equation (11), that is,

$$\pi = \int (\pi_1 . \pi_2 , ...\pi_{n-k}) \tag{12}$$

This equation is the final result of the dimensional analysis. When a complete relationship between dimensional physical quantities is expressed in dimensionless form, the number of independent quantities that appear in it is reduced from the original *n* to *n-k*, where *k* is the maximum number of the original *n* that are dimensionally independent (Sonin, 2001).

The theorem derives its name from Buckingham's use of the symbol π for the dimensionless variables in his original 1914 paper. The π -theorem tells us that, because all complete physical equations must be dimensionally homogeneous, a restatement of any such equation in an appropriate dimensionless form will reduce the number of independent quantities in the problem by *k*. This can simplify the problem enormously, as will be evident from the example that follows (Sonin, 2001).

The π -theorem itself merely tells us the *number* of dimensionless quantities that affect the value of a particular dimensionless dependent variable. It does not tell us the forms of the dimensionless variable. That has to be discovered in the third and fourth steps described above. Nor does the π - theorem, or for that matter dimensional analysis as such, say anything about the form of the functional relationship expressed by Equation (11). That form has to be discovered by experimentation or by solving the problem theoretically.

2.6 Forced-air circulation

In the past, natural convection cooling was used to reduce grape temperature in industry. However, this cooling system is not adequate. Therefore, forced-air circulation was applied since 1995 in order to enhance the velocity and thus the flow rate of the fluid as well as the heat transfer. Later, this system was applied with some other tropical fruit such as mango (Singh et al., 2013) and longan (Jaturonglumlert et al., 2008). The forced-air circulation can be created by an external source such as a fan. In forced-air circulation, fan is the most commonly used to control air and used medium for heat transfer. Air is usually taken directly from surrounding atmosphere and returned to it. There are various types of fans for cooling electronic equipment

which can be divided into two main types, namely axial and centrifugal fans. These fan can be driven by several types of electric motors, single phase, three phase, 60 cycles, 400 cycles, 800 cycles ac/dc, constant speed, variable speed. The flow rate also varies from 1 cfm to several thousand cfm. The fan can be used to draw air through a box or to blow air through a box. A blowing fan system can increase the internal air pressure within the box which will help to keep dust and dirt out of a box that is not well sealed. A blowing system will also produce slightly more turbulence which will improve the heat transfer characteristics within the box

2.6.1 Static pressure and velocity pressure

When there is a difference of pressure between two points in the chamber, airflow will take place by flowing from the high-pressure side to the low-pressure side. The flow of air will result in a static pressure and a velocity pressure. Static pressure is the pressure that is exerted on the walls of the container or chamber, even when there is no flow of air; it is independent of the air velocity. Velocity pressure is the pressure that forces the air to move through the chamber at a certain velocity. The velocity pressure depends on the velocity of the air and always acts in the direction of the airflow. The amount of cooling air flowing through a chamber will generally control the amount of heat removed from the chamber. The higher the air flow rate through the box, the higher heat will be removed. However, it requires an even greater pressure to force the air through the chamber.

The value of static and velocity pressures can be presented in lb.in^{-2} and g.cm^{-2}. Nevertheless, these values are usually very small, so that it is often more convenient to show these pressures in terms of the height of a column of water. The velocity head (H_V) is a convenient reference that is often used to obtain pressure drops through electronic boxes. The velocity head is corresponding to the air flow velocity as follows:

$$V = \sqrt{2_g H_v} \qquad (13)$$

Where: V = Velocity of the air

g = Gravitational acceleration

H_v = Velocity head in centimeter of water

The Equation (13) can be modified using standard air with a density of 0.0012 g.cm^{-3} at 20.5 °C and 1 bar this is shown in Equation (14).

$$V = \sqrt{\frac{2(\frac{979.6cm}{\sec^2})(\frac{1g}{cm^3_{water}})(H_{v.cmwater})}{0.0012g/cm^3_{air}}}$$

$$V = 1277\sqrt{H_{Vwater}} = cm/\sec \qquad (14)$$

The total head will be the sum of the velocity head and the static head as follow

$$H_t = H_V + H_s \qquad (15)$$

2.6.2 Internal forced flow

Heat and mass transfer devices normally comprise of channels, frequently tubes where a fluid is heated, cooled, or changed its configuration. The boundary layers in flow over bodies, such as over a flat plate, can create freely not including impact form adjacent limits, in channels it is fully enclosed and so the boundary layer cannot develop freely. In the following the flow, and then the heat and mass transfer in tube will be discussed (Baehr and Stephan, 2011).

2.6.3 Laminar and turbulent flow

Fluid flows could be divided into two unique categories, namely laminar flows and turbulent flows. Laminar flow could be created when the fluid flows in insignificant parallel layers with no interference between them. For laminar flows, fluid layers slide in parallel, without spins or currents. It is also stated to as streamline flow for the reason that it is categorized by non-crossing streamlines. The laminar flow system is commanded by momentum diffusion, while the momentum convection is less crucial.

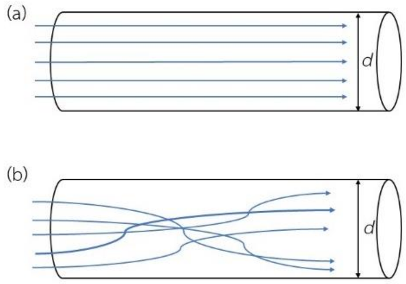


Figure 8 (a) Laminar flow in a closed pipe, (b) Turbulent flow in a closed pipe
Source: Simscale (2020)

In the 19th century, Osborne Reynolds was the first person who published the difference between turbulent and laminar characteristic. This reported was supported by the experimental results according to the transition of laminar to the turbulent system (Reynolds, 1883; Simscale, 2020). The Reynolds number is a macroscopic parameter of a flow in that could be defined as follows:

$$\mathrm{Re} = \frac{\rho \vartheta L}{\mu} \qquad (16)$$

where: ρ is the density of the fluid
ϑ is the macroscopic velocity of the fluid
L is the characteristic length of the involved phenomenon
μ is the dynamic viscosity of the fluid

To divide 2 types of flow, RE was used to separated. The laminar flow will be created at low RE value while turbulent flow will be created at high RE value. The Re number between these laminar and turbulent regions called “transition regime” while the mean of Re in the transition regime is typically called “critical Reynolds number”. Both geometrical properties of the application and material properties of the fluid result in Re number. The correlation between the RE and the regime found in various situation is shown in Table 10 (Reynolds, 1883; Simscale, 2020).

Table 10 Reynolds number and different flow regimes

Problem Configuration	Laminar regime	Transition regime	Turbulent regime
Flow around a foil parallel to the main flow	$Re < 5 \times 10^5$	$5 \times 10^5 < Re < 5 \times 10^5$	$Re > 10^7$
Flow around a cylinder whose axis is perpendicular to the main flow	$Re < 2 \times 10^5$	$Re \approx 2 \times 10^5$	$Re > 2 \times 10^5$
Flow around a sphere	$Re < 2 \times 10^5$	$Re \approx 2 \times 10^5$	$Re > 2 \times 10^5$
Flow inside a circular-section pipe	$Re < 2300$	$2300 < Re < 4000$	$Re > 4000$

Source : Simscale (2020)

2.7 Literature review

2.7.1 Pesticide residues in chili

Burleigh et al. (1998) reported the use of pesticide for chili planting in northeast part of Sri Lanka. It was found that chili farmers in Sri Lanka used a large amount of pesticide while the number of pest did not significantly decrease. Moreover, chili farmers did not wear the appropriate clothes and wearing for their safety.

Ooraikul et al. (2011) evaluated the risk of organophosphate pesticides through the consumption of chili. One hundred and ten people including 65 females and 45 males from Hua Rua agricultural community, Hua Rua sub-district, Muang district, Ubon Ratchathani province, Thailand, were selected for the study. Face-to-face interview was used for the socio-demographic and dietary survey. From the interview, it was found that average chili consumption quantity was 0.018 kg/day which was 3 times more than the average of general Thais of 0.005 kg/day. For the determination of pesticide residues of chili samples, thirty-three chili were sampled from chili farm after they were applied with pesticides for 7 day. Pesticide residues were extracted from chili samples using Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) method. Gas chromatograph equipped with flame photometric detector (FPD) was used for the determination of pesticides quantity. The results showed that 2 types of pesticide residues, namely chlorpyrifos and profenofos, were identified. Moreover, 27% chlorpyrifos and 15% profenofos contaminated samples exceeded the Maximum Residue Limits (MRL) of the Codex Alimentarius (FAO/WHO). Chlorpyrifos and profenofos were generally detected less than the range of 0.010-1.303 $mg.kg^{-1}$ and 0.520-6.290 $mg.kg^{-1}$, respectively. For exposure assessment, an average daily dose (ADD) of chlorpyrifos and profenofos pesticide were found to be 1.07×10^{-4} $mg.kg^{-1}$ -day and 8.00×10^{-4} $mg.kg^{-1}$ -day, respectively.

Taneepanichskul et al. (2014) reported the organophosphate pesticide exposure and dialkyl phospahate urinary metabolites among chili farmers in northeastern Thailand. Chlorpyrifos and profenofos residues were found on dermal patches, face wipes, and hand wipe samples, while no significant residues were detected on the feet. When individual air sampling procedure was carried out, all air samples detected pesticide residues. Nevertheless, significant relationship concerning dermal pesticide exposure concentration and inhalation was not found ($p>0.05$). For urinary metabolite levels, the first pre application morning void corresponded to post application morning void ($p<0.05$); related to the relationship between the first pre application morning void and the second post application morning void ($p<0.05$). The important association between pesticide exposure and urinary metabolite was found to be related to dermal exposure ($r= 0.405$; $p<0.05$).

Ditya et al. (2010) studied the degradation of chlorfenapyr pesticide in chili, cabbage and soil. Chlorfenapyr, 4bromo-2-(4-chlorophenyl)-1-ethoxymethyl-5-trifluoromethyl1H-pyrrole-3-carbonitrile, is a pestiticide that belongs to pyrrole group. It is generally used to prevent caterpillars, mites, aphids, whitefly, leafminers, thrips, etc. In this study, of chlorfenapyr pesticide was applied in chili and cabbage. From the result, the degradation of chlorfenapyr in chili, cabbage and soil was found to be the first-order kinetics ($\log C/C0 =-kt$). The half-lives of chlorfenapyr in chili, cabbage and soil were found to be in the range of 2.93 - 2.96 days, 2.98 - 3.62 days and 4.06 - 4.36 days, respectively.

Swarnam and Velmurugan (2013) reported the determination of pesticide residue in vegetable samples including brinjal, okra, green chilli, crucifers, and cucurbits using a gas chromatograph equipped with electron capture and flame thermionic detectors. The results showed that there were organochlorine (OC), organophosphorus (OP), and synthetic pyrethroid pesticide residue in the samples. OP residues such as chlorpyrifos, profenofos, monocrotophos, triazophos, ethion, dimethoate, and acephate were found in 54 % of the samples with residues, which were taken from all vegetable samples. For the positive samples, 15.3 % were found to contain residues exceeding the prescribed maximum residue limit. The average pesticide residue content across all the vegetable samples was 0.108 ppm, with values in the range of 0.008 to 2.099 ppm. In addition, multiple residues of more than one compound were detected in 34.1 % of samples containing residues.

Siriwong et al. (2011) presented health risk assessment of organophosphate pesticides exposure associated with dermal exposure in chilli-growing farmers. The experiment was carried out during growing season from December 2009 to January 2010 at one of the biggest area for chilli farm in Thailand located in Ubon Ratchathani province, Northeastern, Thailand. From 330 chilli-growing farmer interviews, ther organophosphate insecticides, e.g, profenofos and chlorpyrifos were typically used in this area. The mean concentration of profenofos and chlorpyrifos of 5.89 and 6.95 mg.kg^{-1} was found in the chili farming. It was very dangerous to health and make residue in crop, soil and environment.

Blankson et al. (2016) determined pesticide residues in 155 domestic samples of vegetables collected from local markets in Greater Accra region, Ghana. The results showed that 52% of samples were contaminated with 21 pesticides residues, including organophosphorus and synthetic pyrethroids.

2.7.2 Effect of drying process on pesticide degradation

Cabras et al. (1998) studied the effect of drying technique to the pesticide residues degradation in apricot fruit. Two drying techniques were studied namely sunlight and oven drying. The pesticide bitertanol, diazinon, iprodione, phosalone, and procymidone of apricots were evaluated. The apricot samples were applied with pesticide before one week of the harvest. Then they were dried with sunlight and oven. After one week of pesticide application to apricot farm, diazinon was found to be 100% degraded, while the other pesticides at pre-harvest time showed pesticide remains 50% below MRLs. The degradation of pesticides corresponded with pseudo-first-order kinetics reaction. Moreover, it showed half-lives in the range of 9.1 to 24.4 days. The sunlight- and oven-drying technique resulted in the fruit to concentrate by approximately 6 times. On the other hand, the pesticide residues existing in the fresh apricots were found to be higher than in the dried apricots. In addition, the residue reductions were lower in the oven technique than in the sunlight technique.

Noh et al. (2015) evaluated the effects of drying process on 9 pesticides in chili, consisting of chlorfenapyr, folpet, clothianidin, indoxacarb, diethofencarb, methoxyfenozide, imidacloprid, methomyl, and tetraconazole. After drying process, pesticide residues of clothianidin, diethofencarb, imidacloprid, and tetraconazole reduced in the range of 37–49%. For methomyl and methoxyfenozide, pesticide residue after drying process reduced 16 and 22%, respectively. However, drying process did not affect the amount of chlorfenapyr, folpet, and indoxacarb residues.

Ozbey and Uygun (2006) reported the effect of drying process on organophosphorus pesticide residues in peppermint (Mentha piperita L.). Pesticide free peppermint leaves was saturated in mix pesticides solution in order to let diffusion of pesticides into peppermint leaves. After that, peppermint leaves were kept at 20± 2°C under shade to let it dry naturally for 10 days. The reduction of moisture content was decreased from 85% to 10.4 %. The pesticides residues degradation was considered to be pseudo-first order kinetic reaction. Moreover, half-lives of chlorpyrifos, fenitrothion, malathion, pirimiphos-ethyl were found to be 2.55, 3.24, 2.55 and 4.01 days, respectively.

Ozbey et al. (2017) studied drying effect to pesticides degradation kinetics of chlorpyrifos, diazinon, dimethoate and methidathion pesticides on grape samples. Grapes were dried under two conditions, namely, by sunlight drying for 21 days and in a ventilated oven drying at different temperatures, including at 50 °C for 72 h, at 60 °C for 60 h, at 70 °C for 48 h, and at 80°C for 36 h. During sun drying, half-lives of chlorpyrifos, diazinon and methidathion were 5.64, 6.42 and 5.25 days, respectively. During oven-drying, the pesticides followed the first order kinetic model. When the temperature increased, degradation of pesticides increased.

Pathan et al. (2009) reported the effect of drying process on pesticide residues, consisting of dicofol, ethion, and cypermethrin, in chili. The experimental results showed that initial residues of dicofol, ethion and cypermethrin in fresh chili were 0.72, 0.40 and 0.02 $mg.kg^{-1}$, respectively. While in sundried chili powder, residues of dicofol, ethion and cypermethrin were 4.03, 1.41 and 0.15 $mg.kg^{-1}$. In addition, it was found that after drying process of the fresh chili, the weight decreased by 10.48 times, while the concentration of dicofol, ethion and cypermethrin raised by 5.59, 3.52 and 7.50 times, respectively.

Cabras and Angioni (2000) studied the behavior of pesticide residues on grapes from treatment to harvest and their fate in drying, wine-making, and alcoholic beverage processing. The degradation rate of certain insecticides in fresh grapes exhibited very rapid rate with $t_{1/2}$ in the range of 0.97-3.84 days. After the drying process, insecticides were determined in a fruit with concentration of 4 times less than fresh grapes. However, some kinds of insecticides residue such as benalaxyl, phosalone, metalaxyl, and procymidone on sun-dried grapes remained the same amount as those on the fresh grape.

Liu et al. (2016) examined the pesticide contamination of six pesticides (carbendazim, thiabendazole, procymidone, bifenthrin, λ-cyhalothrin, and β-cyfluthrin) in shiitakes from cultivation to postharvest drying process. Under sundrying, six pesticide showed degradation half-life at 12.6, 8.8, 11.3, 18.1 29.3 and 19.4days, respectively. Conversely, under hot-air drying process, the degradation half-life of six pesticide residues was 26.6, 16.1, 18.6, 25.3, 45.4 and 33.2 h. The results showed that hot-air drying resulted in greater residues degradation than sunlight exposure drying.

2.7.3 Effect of ozone on pesticide degradation

Fernanda et al. (2014) determined the effect of ozone fumigation on the reduction of difenoconazole residue on strawberries. Firstly, strawberries were soaked in difenoconazole pesticide. Then, they were dried and fumigated by ozone gas. The results showed that 95% of difenoconazole residue could be decreased after the fumigation.

Whangchai et al. (2011) evaluated the effect of ozone on the reduction of chlorpyrifos residue in lychee cv. Chakapat (Litchi chinensis Sonn.). Lychee fruits were soaked in chlorpyrifos solution. Then, they were fumigated with ozone gas or soaked in ozone–containing water. Both ozone gas and ozone–containing water reduced pesticide residue in lychee. Fumigation with ozone gas for 60 min was most effective. Moreover, ozone-containing water reduced the eating quality of lychees after storage when compared with the ozone gas fumigation.

Kusvuran et al. (2012) presented ozonation technique to remove chlorothalonil, tetradifon, and chloropyrifos ethyl pesticide residues from the lemon, orange, and grapefruit. All chlorothalonil residues adsorbed onto the orange were entirely degraded ozonation for 5 min. The greatest degradation percentages of tetradifon and chlorpyrifos ethyl were completed as 98.6 and 94.2%, respectively for the lemon and grapefruit. After 5 min ozonation, the entire diffused chloropyrifos ethyl and chlorothalonil residues were completely removed from both grapefruit and orange. This research revealed that increasing of ozone dosage applying to the system was not significantly effect on the removal percentages of pesticides. Furthermore, ozonation temperature resulted in a reducing of the pesticides removal percentages. Also, the cleaning process of fruit with tap water in this experiment was not able to remove pesticides residues effectively. The results revealed that ozonation process exhibited excellent performance for pesticide removal in fresh fruits such as grapefruit, orange, and lemon.

Lozowicka et al. (2016) also reported on effect of ozone water washing process to pesticide degradation compared with ultrasonic cleaning and boiling process. In this research, 16 pesticides, including ten fungicides and six insecticides, in fresh strawberries were examined. Gas chromatography with nitrogen-phosphorous and electron capture detection (GC-NPD/ECD) was conducted for the analysis of these pesticides. The processing factor (PF) for each pesticide in each processing technique was determined. Cleaning with ozonated water was proven to be more efficient (decrease by 36.1 -75.1 %) than washing with tap water (decrease by 19.8- 68.1 %). Boiling lessened the pesticides of the most substances, decreasing in the range of 42.8-92.9 %. Ultrasonic cleaning decreased all pesticides up to 91.2 % degradation.

Ikeura et al. (2011) showed the degradation of fenitrothion pesticide residues from vegetables by soaking in ozone-microbubbled solution. Lettuce, cherry tomatoes, and strawberries which were contaminated with pesticides were soaked in ozone-microbubbled, ozone-millibubbled, and dechlorinated water. Subsequently, the percentage of fenitrothion pesticide residues in the vegetables was analyzed. Fenitrothion pesticide residues was degraded from lettuce by soaking in 1.0 ppm ozone-microbubbled solution, or 2.0 ppm continuously generated ozone-microbubbled solution, efficiently. Correspondingly, for cherry tomatoes and strawberries, the 2.0 ppm continuously generated ozone-microbubbled solution showed the huge degradation of fenitrothion pesticide residues.

2.7.4 Forced-air fumigation

Jaturonglumlert et al. (2008) improved SO_2 fumigation in fresh longan by applying a vertical forced-air. SO_2 concentration at 10,000 – 12,000 ppm was circulated through the forced-air column inside fumigation chamber for 60 min. After fumigation the concentration of SO_2 residue was within range 1,600 – 1,800 ppm. The SO_2 gas concentration reduce to final concentration at 4000 ppm. The fumigated sample was stored at 2 °C/95% RH. The result show that the forced-air fumigation effectively prevented postharvest disease and browning for at least 20 days. The vertical forced-air can reduce initial concentration of SO_2 from official recommendation approximately 3-5 times.

Defraeye et al. (2014) reported the effect of two new design exiting container for orange fruit on force convective precooling using computational fluid dynamic. The main focus of this study was fruit cooling rate and the system energy consumption. The new package design both showed an improved cooling rate and cooling uniformly.

The energy usage depends on air flow thought the container and aerodynamic resistance. This new container seem to be a cost-effective way for improving forced convection precooling of orange fruit with respect to throughput, fruit quality and operational cost of system.

Anderson et al. (2004) reported the effect of difference clamshell container and pallet arrangement on the cooling rate. The clamshell design had a significant effect. It can be concluded that the vent-hole design plays a significant role on the forced-air cooling time. In addition, 6-down configuration was significantly faster than 5-down configuration. Therefore, the clamshell container and pallet arrangement should be designed together to maximize air - to – product contact during cooling process.

Vigneault and Goyette (2002) reported the development of containers for precooling fruits and vegetable crops with forced-air precooling technique. Forced–air cooling was carried out by forcing cold air through stacked containers and passed through individual pieces of fruits. This allowed the creation of a pressure gradient throughout the package containers, generating a driving force to draw air from the surrounding.

Zhou et al. (2006) stated that pre-cooling is the crucial factor in the circulation system of fruits and vegetables. It is also the earlier procedure in the cold chain. Rapid refrigerating has been evidently proven to extend the storage lifetime of fresh harvested product. Forced-air cooling is the most adaptable and commonly utilized of all cooling techniques.

From the literature reviews, it was found that a large amount of pesticides has been used in chili farming in order to protect the crop production losses caused by pest. From the report, the amount of pesticide contaminated in chili exceeded the acceptable limits. Even though chili was dried with sunlight, pesticide contamination was detected. Therefore, pesticide degradation should be carried out. In this work, ozone fumigation is selected to use as a pesticide degradation technique. From literature reviews, as shown in Table 11 and 12, pesticide residue degradation depended on ozone concentration, contact time, and especially pesticide residue concentration which used in various experiment ranging from 0.15 – 5 $mg.kg^{-1}$. In addition, ozone self-degradation period is short. Thus, this technique does not leave any harmful residue on the treated products. In order to improve the efficiency of ozone fumigation, forced-air circulation is used to increase the flow rate, air distribution, reduce initial ozone concentration of ozone gas that allow gas to react with the surface of product.

Table 11 Summary of literature reviews of ozone and pesticide residue

Pesticide name / fruit or vegetable	Condition of ozone application	Results	References
Difenoconazole residue in strawberries	Ozone fumigation at concentration 0.3, 0.6 and 0.8 mg.L^{-1} for 1 hr. Initial concentration at 5 mg.kg^{-1}	Difenoconazole degradation increased with increasing of ozone concentration with maximum percentage of 95%.	Heleno, Fernanda F et al. (2014)
Chlorpyrifos residue in lychee	Ozone fumigation at concentration 240 mg.L^{-1} and Ozonated water at concentration 3.2 mg.L-1 for 10, 20, 30 60 min.	Ozone fumigation and ozonated water can remove chlorpyrifos up to 45% and 10.3 %, respectively.	Whangchai et al. (2011)
Chlorpyrifos ethyl, tetradifon and chlorothalonil pesticide residues in the lemon, orange, and grapefruit	Ozonated water concentration = 4, 6 and 10 mg.L^{-1} Temperature = 10, 20 and 40 C Time = 5 min Initial concentration of residue = 0.15 mg.kg^{-1}	Pesticides degradation increased with increasing of ozone concentration and decreasing of degradation temperature.	Kusvuran et al. (2012)
16 pesticide, including 10 fungicides and 6 insecticides, in fresh strawberries	Ozonated water concentration = 1mg.L^{-1} Time = 1, 2 and 5 min Initial concentration of residue = 3.00 mg.kg-1	Ozonated water was proven to be efficient in pesticides degradation with percentage ranging from 36.1 -75.1 %.	Lozowicka et al. (2016)
Fenitrothion residues in lettuce, cherry tomatoes, and strawberries	Ozonated micro bubble concentration = 0.5 – 2.0 mg.L^{-1} Time = 10 min Initial concentration for residue = 100-200 mg.kg^{-1}	Pesticides degradation increased with increasing of ozone microbubble concentration in all types of vegetables.	Ikeura et al. (2011)

Table 12 Summary of literature reviews of forced-air circulation

Application	Key Results	References
Improvement of SO_2 fumigation in fresh longan by applying a vertical forced-air using SO_2 concentration at 10,000 – 12,000 ppm	The vertical forced-air can reduce initial concentration of SO_2 from official recommendation approximately 3-5 times.	Jaturonglumlert et al. (2008)
Design of new container for improvement of cooling rate and cooling uniformity of orange fruit	Forced – air convection can improve precooling process of orange fruit with respect to throughput, fruit quality and operational cost of system.	Defraeye et al. (2014)
Improvement of strawberries packaged in clamshell containers with a variety of tray designs precooled in commercial cooling systems by force air cooling	The clamshell design had a significant effect on cooling rate when used in the same tray design and cooling rate depend on pallet orientations.	Anderson et al. (2004)
Development of containers for precooling fruits and vegetable crops with forced-air precooling technique	Pressure drop inside container is an important parameter in forced-air circulation technique and opening widths of 3.2 to 12.7 mm on the surface of the containers have a negligible effect on pressure drop during air circulation through container walls.	Vigneault and Goyette (2002)
Development of pre-cooling system for fruits and vegetables with forced-air circulation	Forced- air cooling is the most adaptable and commonly utilized of all cooling techniques.	Zhou et al. (2006)

CHAPTER 3

RESEARCH METHODOLOGY

The study of pesticides residues degradation using ozone fumigation coupled with forced-air circulation system was divided into 2 parts as shown in Figure 9.

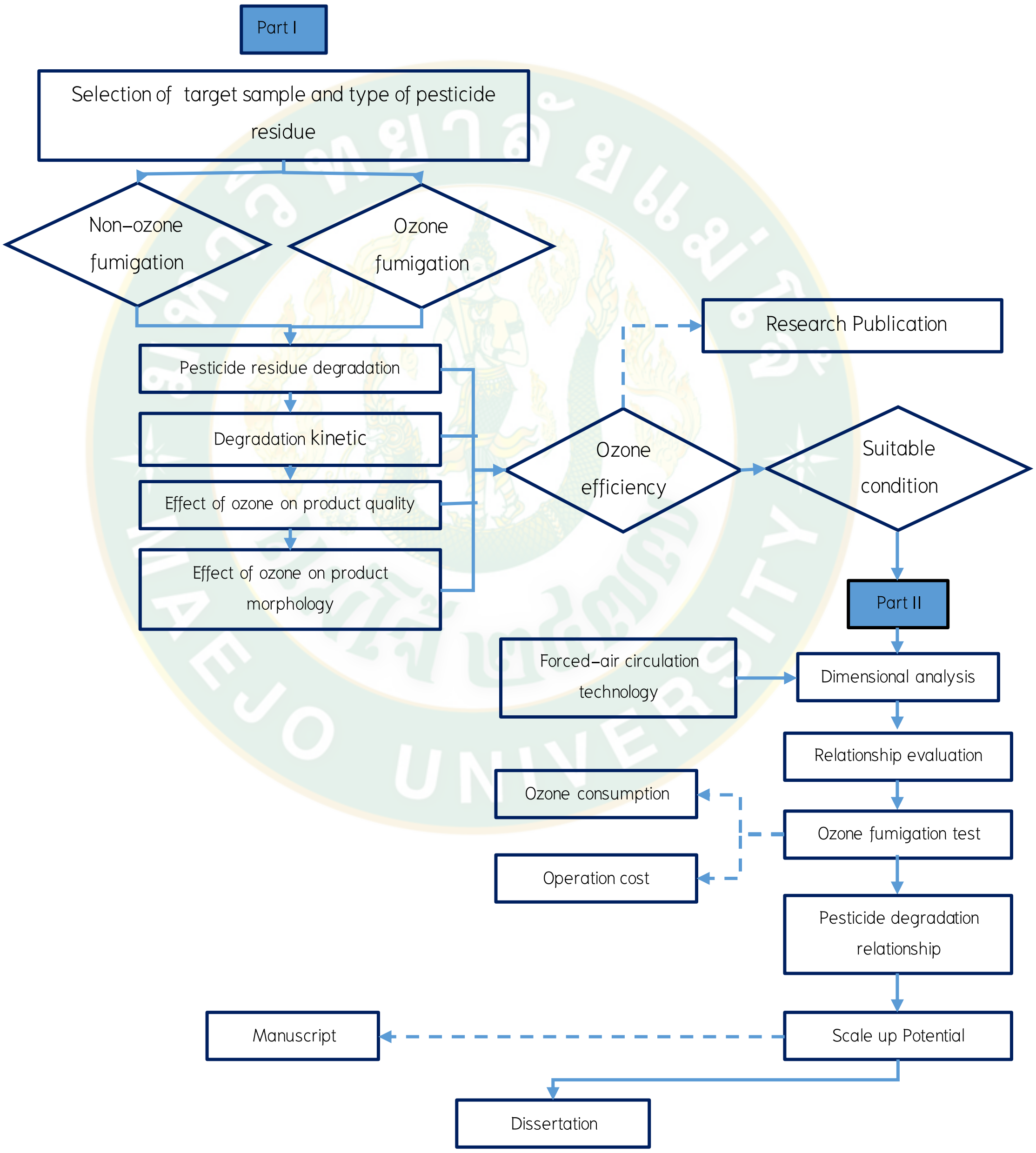


Figure 9 Research diagram and framework.

3.1 Part 1: Pesticides degradation in dried chili under gaseous ozone fumigation.

The objective of part 1 was to study the pesticides degradation efficiency on dried chili under gaseous ozone fumigation and the effect of gaseous ozone fumigation to physical and chemical properties of dried chili. Therefore, the experimental method was set up to compare pesticides degradation between non-ozone and ozone fumigation assisted accordingly. Physical and chemical properties of dried chili were then evaluated to ensure that ozone fumigation did not affect to chili qualities.

3.1.1 Non-ozone fumigation and self-degradation of pesticides

3.1.1.1 Pesticide treatments of dried chili samples

Red dried chili samples were purchased from local market in Chiang Mai, Thailand. Ten of dried chili was batched and sprayed with 20 mL using 1000 mg.L^{-1} pesticide mixture namely Diazinon, Malathion, Chlorpyrifos, Profenofos, Ethion and Triazophos. The sample was air dried at 25 C for 10 h and packed in a low density poly ethylene bags and stored at 25 °C. The pesticide - contaminated chili was analyzed every 7 days throughout a storage period for 8 weeks.

3.1.1.2 Determination of pesticide residue

The extraction of pesticide residue was performed with acetonitrile and NaCl solutions and cleanup sorbents used in dispersive solid phase extraction, following the QuEChERS method (Grimalt and Dehouck, 2016). The 40 mL of acetonitrile (AR grades, RCI labscan, Thailand) was added into 10 g of dried chili. Then, they were homogenized at 20,000 rpm for 2 min. The volume of samples was diluted to 50 mL with acetonitrile. The sample was shaken together with 5 grams of anhydrous magnesium sulphate and 1.5 g of sodium chloride for 1 min. The supernatant was transferred to a 50 mL centrifuge tube, containing 0.2 g of primary secondary amine (PSA), 3.0 g of anhydrous magnesium sulphate, and 0.2 g of activated charcoal for cleanup. The extract was centrifuged at 2,500 rpm for another 10 min. The 10 mL of supernatant was transferred to test tube and evaporated by nitrogen evaporator. The volume of sample was adjusted to be 5 mL by ethylacetate and filtered thought the 0.45 µm nylon membrane filter to 2 mL vial. Pesticide residue were analyzed by gas chromatograph equipped with flame photometric detector (GC-FPD), model 6890N, (Agilent Technologies Canada Inc.) using HP-5 capillary column with 0.255 µm-particle size, and 30 m x 0.32 mm (i.d.). Helium gas was used as a carrier gas with a flow rate of 1.5 $mL.min^{-1}$. The temperature and heating rate were performed following the steps show in Table 13.

Table 13 Oven temperature program for GC-FPD determination of pesticide residue

Step	Action	Condition	Heating rate
1	Initial	80 °C for 2 min	
2	Ramp up I	150 °C for 5 min	25°C.min^{-1}
3	Ramp up II	190 °C for 5 min	5°C.min^{-1}
4	Ramp up III	220 °C for 5 min	10°C.min^{-1}
5	Final	250°C	10°C.min^{-1}

3.1.2 Effect of ozone fumigation time on the degradation of pesticide

3.1.2.1 Pesticide treatments of dried chili samples

Red dried chili was obtained from local market in Chiang Mai Thailand. The 10 kg of dried chili was sprayed with 20 mL of pesticide mixture solution containing 1000 $mg.L^{-1}$ of pesticide namely Diazinon, Malathion, Chlorpyrifos, Profenofos, Ethion and Triazophos. The sample was dried in air for 10 h.

3.1.2.2 Ozone fumigation process

Five hundred grams of red dried chili were packed in a 25 Litre-polycarbonate container for ozone fumigation as shown in Figure 10. Gaseous ozone will be generated by ozone generator using corona discharge equipment. The pesticides-treated dried chili was fumigated with ozone. The chili sample with ozone fumigation was packed in low density polyethylene bag and was stored at 25 °C for 8 weeks to compared with non-ozone treatment for pesticide degradation.

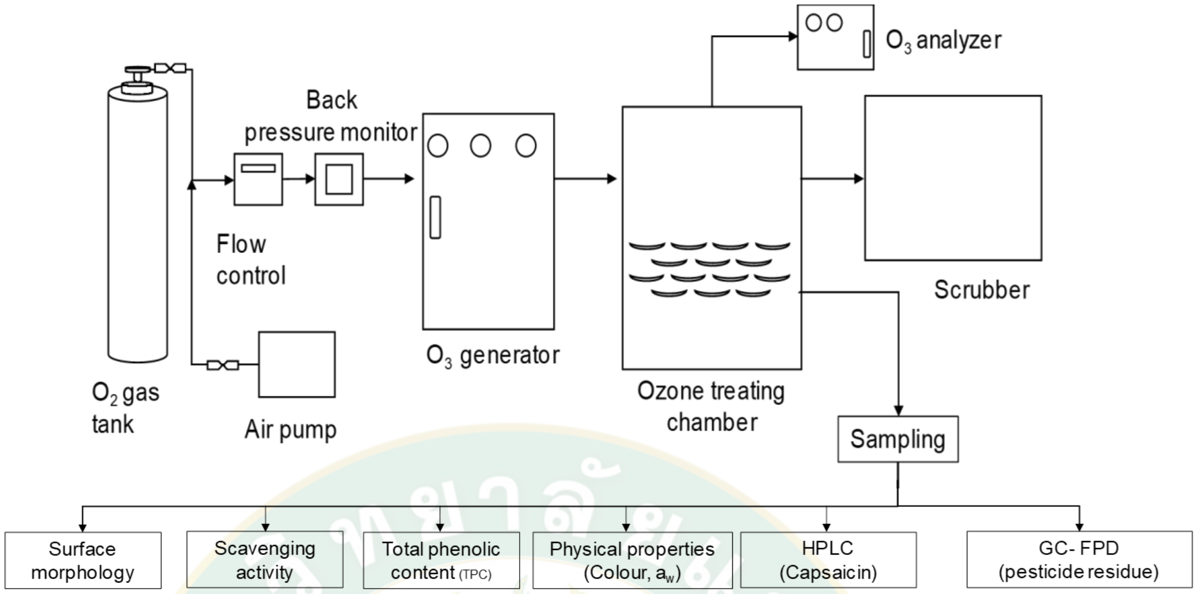


Figure 10 Schematic diagram of gaseous ozone fumigation process

3.1.2.3 Determination of pesticide residue

The extraction of sample and the determination of pesticide residue were performed as mentioned in 3.1.1.2.

3.1.2.4 Determination of pesticide degradation kinetics

The integrated rate law can be used to examine the reaction kinetics order from obtained experimental data. The basic patterns used to classify the reaction order are described in zero, first and second order kinetics.

3.1.2.5 Measurement of physical properties

Water activity was measured using an AquaLab water activity meter (Model 3TE, Decagon devices, USA). The experimental data was obtained from 3 replications. For color measurements, all samples were cut lengthwise and spread out to evaluate the color of the chili peel using a Hunter Lab Colorflex colorimeter. Instrumental color data were analyzed using the CIE system in terms of L* (lightness), a* (redness and greenness) and b* (yellowness and blueness).

3.1.2.6 Capsaicin content

The chili was extracted using the modified method from Collins *et al.* (1995). For capsaicin extraction, the 40 mL of acetonitrile (AR grades, RCI labscan, Thailand) was added into 10 g of each dried chili. Then, they were homogenized at 20,000 rpm for 2 min. The volume of samples was diluted to 50 mL with acetonitrile. All samples will be kept at 4 - 8 °C for 24 h. Finally, the supernatant layer of each sample was filtered through 0.45 µm-nylon filter paper into a vial using a 2 mL disposable syringe (Millipore, Bedford, MA, USA). The capsaicin analysis was carried out by high-performance liquid chromatograph (HPLC, 1100 Series, Agilent Technologies Canada Inc.) with a UV-diode array detector (UV-DAD) at 274 nm. The separation was achieved using a ZORBAX *Eclipse XDB* C-18 reverse-phase column (5 µm particle size, and 150 mm x 4.6mm (i.d.), Agilent Technologies Canada Inc.) and 10 µL of extract was automatically injected into the system and was eluted using an isocratic mobile phase (acetonitrile/DI water 70:30 (v/v)) at 1 mL.min^{-1} flow rate.

3.1.2.7 Total phenolic content (TPC)

The TPC was studied using the modified method of Folin-Ciocalteu assay (Kovacova and MaliNoVá, 2007). Firstly, methanolic extract solution was prepared by mixing the 5 g of sample with 20 ml of 70% methanol. The mixture was kept overnight at -20 °C. Then the sample was adjusted to final volume of 50 ml and was centrifuged at 2,500 rpm at 4°C for 10 min. The 0.5 ml of 50% Folin-Ciocalteu, 1 mL of 95% ethanol, 1 mL of methanolic extract, and 5 mL of reverse osmosis water were mixed and kept at room temperature (25±5 °C) for 5 min. After that, 1 mL of 5% (w/v) of sodium carbonate solution was added. The mixture was homogenized and kept at room temperature for another 60 min. The TPC was analyzed using a spectrophotometer model NICOLET evolution 300 (Thermo Electron Eorporation, USA) at 725 nm. The standard calibration curve was plotted using gallic acid at the concentration of 10 – 200 mg.L^{-1}. The TPC was presented as gallic acid equivalent (GAE) in a unit of mg.100 g^{-1}.

3.1.2.8 Free radical scavenging activity

Determination of scavenging activity of dried chili extract was carried out based on 2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical scavenging assay (Milardović et al., 2006). The 2 mL of chili extract was mixed with 1 mL of 100 µM DPPH solution which dissolved in 80% methanol. The mixture was then shaken vigorously and kept in a dark room for 30 min at room temperature. The absorbance was evaluated using a spectrophotometer (Thermo Electron Corporation, NICOLET evolution 300, USA). The detection was determined at 515 nm of wavelength using methanol as a blank solution. Triplicate analysis were done and their activity was expressed as Trolox equivalent (TEAE) in mg/100 g^{-1}.

3.1.2.9 Microstructure of dried chili

Scanning electron microscopy (SEM) technique was used to examine microstructure of chili surface without and with ozone fumigation for 30 min. The dried chili peel was cut into a small piece (5x5 mm). The sample was coated with gold 20 nm thick gold in the ion sputter coater model JFC-1200 (JEOL, Japan). The microstructure of chili surface was observed by SEM model JSM-5410LV (JEOL, Japan) at 10 kV.

3.1.2.10 Statistical analysis

In this experiment, the data were statistically examined using the Statistics Package for the Social Sciences (SPSS, IBM Corp., USA) using one-way analysis of variance (ANOVA). Duncan's test was used for statistical analysis. The significant difference of responses was determined at 95% confident level ($p<0.05$).

3.2 Part 2: Parameters affecting ozone fumigation using vertical forced-air (VFA) technique

The objective of part 2 was to develop gaseous ozone fumigation on dried chili using a novel VFA technique. Therefore, pressure drop across basket stack was determined and applied in the pesticide residue degradation on dried chili treated by ozone-VFA fumigation to design a future industrial application.

3.2.1 Pressure drop across basket stack

Pressure drop is an important parameter indicating the gas distribution in chamber containing died chili basket. Good gas distribution results in the low pressure drop. There are several parameters affecting pressure drop in the chamber, namely air flow rate, air velocity, cross-sectional area of basket and chili load. Therefore, relationship between forced–air circulation parameters and pressure drop of basket stack was determined in order to evaluate dimensional analysis using Buckingham's π theorem on dry chili's basket stacking when apply vertical forced-air ozone fumigation.

3.2.1.1 Air flow rate and air velocity distribution

3.2.1.1.1 Effect of air flow rate in VFA system was studied. In this experiment, 5 chili baskets were stacked vertically in the 248 L-fumigation chamber with upward air-flow direction as shown in Table 23 and Figure 13. Air flow rate of forced-air circulation system was regulated by the input voltage of fan of 60, 90, 120, 150, 180 and 210 V. Air velocity was measured 9 points (Figure 12) in total for calculation of average air velocity in order to obtain air flow rate using Equation 17.

$$Q = AV \tag{17}$$

Where: Q = air flow rate ($m^3.s^{-1}$)

A = cross-section area of testing tube which is used for air flow rate test (m^2)

V = average of air velocity (m/s) at distance of 1.50 m from fan (Figure 11)

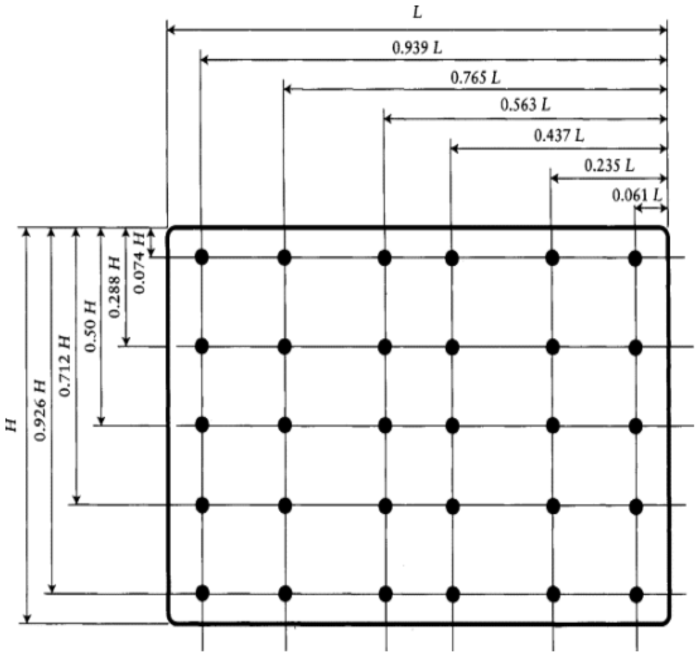


Figure 11 Air velocity measuring point per diameter

Source : ASHREA, 2001

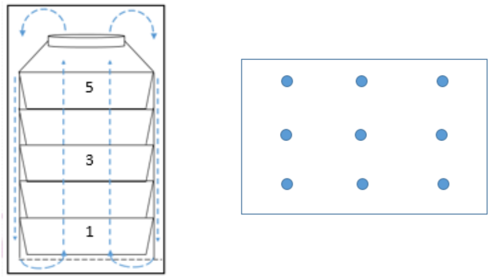


Figure 12 The 5-layer basket stacking and velocity measurement point in the experiment.

3.2.1.1.2 Air velocity in VFA chamber was measured at nine point of the 1st, 3rd and 5th layers of basket as shown in Figure 12. An average air velocity was used to calculate the air flow through cross-section of the basket. A standard deviations (SD) of air velocity was determined at various air flow rate in order to identify the variation of air velocity measurement.

3.2.1.2 Air flow rate and pressure drop

The typical air flow rate was selected to further measure the pressure drop using differential pressure meter (Testo 510, USA). The difference in pressure between bottom basket (P_0) and each designated basket layer (P_1, P_3, P_5) were determined as shown in Figure 13. The air flow rate which resulted in the least pressure drop was selected for pesticide degradation analysis in 3.1.1.2.

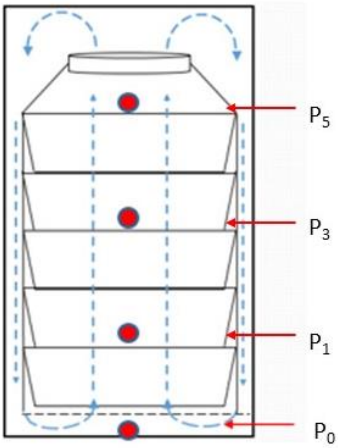


Figure 13 Diagram of the determination of pressure drop between basket bottom (P_0) and each basket layer (P_1, P_3, P_5)

3.2.1.3 Dimensional analysis

Dimensional analysis was carried out using Buckingham's π theorem base on affective parameters as shown in Table 14. The relationship between these parameters are given as Equation 18.

$$\Delta P = \int(\rho, \frac{C}{C_0}, \mu, v_s, A, \varepsilon_v, L) \tag{18}$$

Table 14 Parameters affecting pressure drop between chili basket stack and stacking dimension

Variable	Symbol	Unit	Dimensions symbol
Pressure drop	ΔP	$Kgm^{-1}s^{-2}$	$ML^{-1}t^{-2}$
Density	ρ	kgm^{-3}	ML^{-3}
Concentration ratio	C/C_0	-	-
Viscosity	μ	$Kgm^{-1}s^{-1}$	$ML^{-1}t^{-1}$
Superficial velocity	v_s	$m.s^{-1}$	Lt^{-1}
Flow area	A	m^2	L^2
Volume void factor	ε_v	-	-
Stack hight	L	m	L

The Volume void factor (ε_v) is a commonly used term when flow in packed beds. It is defined as Equation (19).

$$\varepsilon_v = \frac{Bed\ volume - Packing\ volume}{Bed\ volume} \tag{19}$$

Superficial velocity (v_s), in the engineering of multiphase flows and flows in porous media. It is defined as Equation (20).

$$v_s = \frac{\dot{m}}{\rho \varepsilon_v A_C} \tag{20}$$

Where $\dot{m}$ = mass flow rate ($kg.s^{-1}$)

ρ = Density of air ($kg.m^{-3}$)

A_c = cross sectional area (m^2)

Velocity of air flow through baskets layers was measured in order to determine correlation between dimensionless numbers (Eu number, Re number, $A.L^{-2}$) and pressure drop (ΔP). Air was flow through the 5 baskets layers with flow rate in the range of 0.09, 0.14, 0.20, 0.26 and 0.32 $m^3.s^{-1}$. Dried chili samples were loaded into baskets with chili load varied from 1, 2, 3, 4, and 5 kg. Each layer of basket contained 1 kg of dried chili samples. Air velocity was measured 9 points in total using hot wire air velocity meter (TENMARS, TM-4002, Taiwan).

3.2.2 Pesticide residue degradation on dried chili treated by ozone-VFA (OVFA) fumigation

3.2.2.1 OVFA fumigation experiment was set up with fuming condition of designated ozone flow obtained from experiment 3.2.1.1

3.2.2.2. Red dried chili was obtained from local market in Chiang Mai Thailand. The batch of 10 kg dried chili was sprayed with 20 mL of pesticide mixture solution containing 1000 $mg.L^{-1}$ of pesticides. The sample was dried in ambient air for 10 h and fumigated in 5-stack fumigation chamber. After fumigation, dried chili in the 1st, 3rd and 5th stacks were sampled, as shown in Figure 14, to determine pesticide residue. The extraction of sample and the determination of pesticide residue were performed as mentioned in 3.1.1.2.

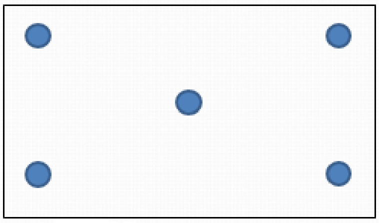


Figure 14 Cross-sectional sampling diagram for pesticide residue determination.

3.2.3 Conceptual design for commercial scale-up

The effective ozone dosage from Part 1 was applied to coupled with VFA in the 3.2.1 to conceptually design the commercial scale fumigation system. To evaluate the efficiency of fumigation chamber, pressure drop and result from dimensional analysis were used in Part 2 to ensure the gas distribution which depends on density (ρ), viscosity (μ), Superficial velocity air velocity (v_s), flow area (A), stack high (L), porosity (ε). Since there are several parameters affecting to pressure drop (∆P), dimensional analysis was carried out to obtain the relationship between dependent and independent parameters. The acquired experimental result was used to scale up from model to prototype. Finally, the effective ozone dosage and fumigation chamber from Part 1 and 2 can be applied to design the conceptual industrial application.

CHAPTER 4

Results and discussion

4.1 Study of pesticides degradation on dried chili under gaseous ozone fumigation

4.1.1 Non – ozone fumigation and self-degradation

The pesticide residue concentration of 6 organophosphate pesticides was sprayed on the chili without ozone fumigation is show in table 15.

Table 15 Pesticide residue concentration of dried chili during a storage period of 8 weeks in ambient temperature

Storage time (week)	Remaining pesticide concentration ($mg.kg^{-1}$)					
	Diazion	**Malathion**	**Chlorpyrifos**	**Profenofos**	**Ethion**	**Triazophos**
0	1.87 ± 0.08	1.94 ± 0.13	1.96 ± 0.14	1.95 ± 0.11	2.05 ± 0.02	1.94 ± 0.20
1	1.78 ± 0.08	1.73 ± 0.14	1.92 ± 0.12	1.86 ± 0.13	2.05 ± 0.05	1.92 ± 0.07
2	1.54 ± 0.07	1.45 ± 0.04	1.79 ± 0.07	1.64 ± 0.10	1.90 ± 0.02	1.95 ± 0.08
3	1.47 ± 0.01	1.34 ± 0.02	1.69 ± 0.08	1.49 ± 0.03	1.87 ± 0.01	1.76 ± 0.02
4	1.44 ± 0.02	1.25 ± 0.03	1.56 ± 0.05	1.48 ± 0.04	1.87 ± 0.01	1.70 ± 0.07
5	1.22 ± 0.09	1.21 ± 0.03	1.54 ± 0.12	1.44 ± 0.06	1.76 ± 0.01	1.56 ± 0.14
6	1.18 ± 0.11	1.16 ± 0.03	1.36 ± 0.02	1.35 ± 0.26	1.72 ± 0.04	1.56 ± 0.23
7	1.20 ± 0.03	1.11 ± 0.01	1.28 ± 0.07	1.20 ± 0.12	1.57 ± 0.01	1.31 ± 0.06
8	1.11 ± 0.01	1.05 ± 0.10	1.20 ± 0.03	1.12 ± 0.04	1.47 ± 0.12	1.19 ± 0.11

*: Data shown represent mean of 2 replications with standard deviation.

It was found that during a storage period of 8 weeks, initial concentration (denote as C_0) of diazinon, malathion, chlorpyrifos, prefenofos, ethion and triazophos pesticide residue was 1.87, 1.94, 1.96, 1.95, 2.05 and 1.94 $mg.kg^{-1}$, respectively. After 8 weeks of storage, the concentration of pesticide residue decayed to 1.11, 1.05, 1.20, 1.22, 1.47 and 1.19 $mg.kg^{-1}$, respectively. The pesticide's self-degradation during storage period was calculated in term of C/C_0, as shown in Table 16 and Figure 15. Where C is the concentration at the given time.

Table 16 Pesticide self-degradation during storage period in term of C/C_0

Storage time (min)	C/C_0					
	Diazion	Malathion	Chlorpyrifos	Profenofos	Ethion	Triazophos
0	1.00	1.00	1.00	1.00	1.00	1.00
10080	0.95	0.89	0.98	0.95	1.00	0.99
20160	0.82	0.75	0.91	0.84	0.93	1.01
30240	0.79	0.69	0.86	0.77	0.91	0.91
40320	0.77	0.64	0.80	0.76	0.91	0.88
50400	0.65	0.62	0.78	0.74	0.86	0.80
60480	0.63	0.60	0.69	0.69	0.84	0.80
70560	0.65	0.57	0.65	0.62	0.77	0.68
80640	0.60	0.54	0.61	0.58	0.72	0.61

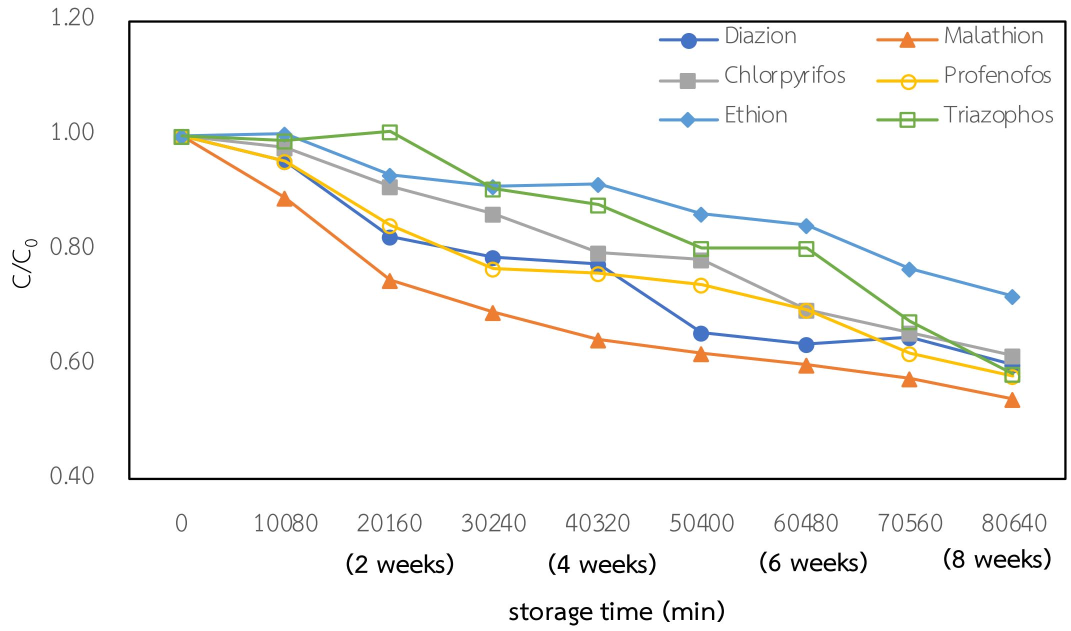


Figure 15 Organophosphate pesticides degradation during storage period at 25°C without ozone fumigation

After 8 weeks in storage, daizinon, malathion, chlorpyrifos, prefenofos, ethion and triazophos were degraded by 41%, 46%, 39%, 42%, 28% and 39%, respectively, as shown in Figure 16. The results revealed that malathion showed the hightest self-degradation percentage up to 46% while ethion showed the lowest self-degradation percentage of 28% compared to other pesticides. The difference in self-degradation performance depends on various factors such as chemical structure, bonding characteristic and strength. The results corresponded with the previous research by Kumar et al. (2018). The authors stated that malathion revealed faster degradation than ethion in the natural environment at 20 C. Degradation of Ethion, for the study of degradation kinetics, the result was presented in terms of ln of remaining concentration pesticide residue in storage period as shown in Table 17.

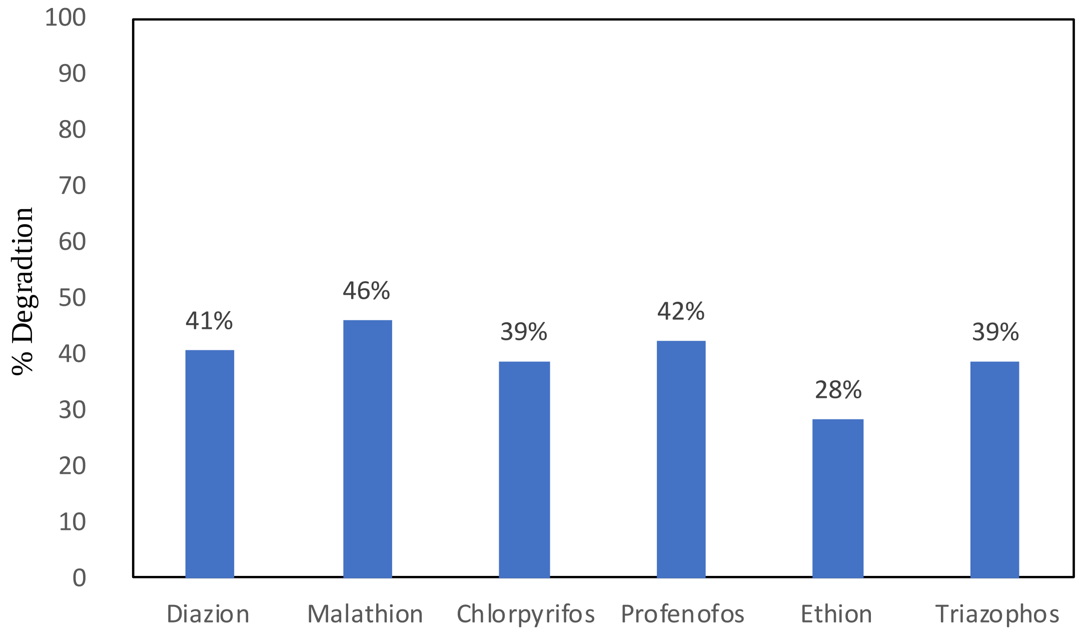


Figure 16 Degradation percentage of Pesticide residue after storage period 8 week.

Table 17 Relationship of ln of pesticide concentration and storage time for 8 weeks in natural logarithm scale.

Storage time (week)	**ln of Remaining pesticide concentration (ln of mg.kg^{-1})**					
	Diazion	**Malathion**	**Chlorpyrifos**	**Profenofos**	**Ethion**	**Triazophos**
0	0.62	0.66	0.67	0.67	0.72	0.66
1	0.58	0.55	0.65	0.62	0.72	0.65
2	0.43	0.37	0.58	0.50	0.64	0.67
3	0.38	0.29	0.53	0.40	0.62	0.56
4	0.37	0.22	0.45	0.39	0.63	0.53
5	0.20	0.19	0.43	0.37	0.57	0.44
6	0.17	0.15	0.31	0.30	0.54	0.44
7	0.19	0.11	0.25	0.19	0.45	0.27
8	0.11	0.05	0.19	0.12	0.38	0.12

For degradation kinetic, The degradation rate contants (k) was determined by creating of relation plot between $\ln_c$ and storage time, as shown in Figure 17. Self-degradation kinetics of all six organophosphate pesticides are considered to be first order reaction. The degradation rate constants (k) of diazinon, malathion, chlorpyrifos, prefenofos, ethion and triazophos on non-ozonated chilis were 7.00×10^{-6}, 7.22×10^{-6}, 6.35×10^{-6}, 6.54×10^{-6}, 3.98×10^{-6} and 6.00×10^{-6} mg.kg^{-1} .min^{-1}, respectively. For the degradation half-life period ($t_{1/2}$), non-ozonated chili revealed the $t_{1/2}$ for diazinon, malathion, chlorpyrifos, prefenofos, ethion and triazophos of 68.8 ,66.6 75.7, 73.5, 120.9 and 80.2 days, respectively.

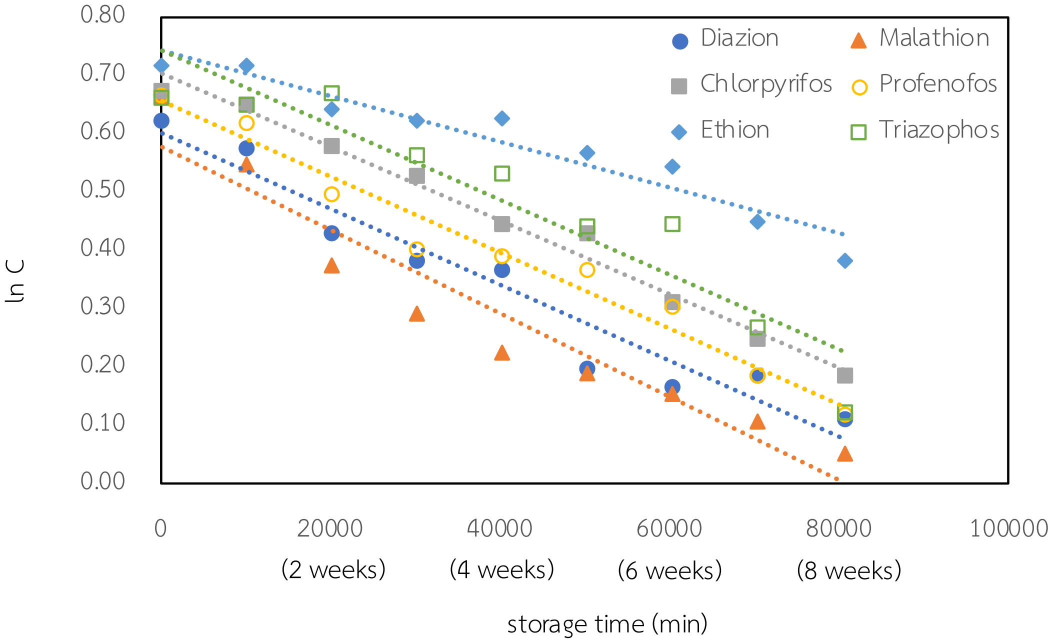


Figure 17 First-order kinetics plot of the organophosphate pesticides degradation during storage at 25°C without ozone fumigation.

4.1.2 Effect of ozone fumigation time on the degradation of pesticide

The degradation of 6 organophosphate pesticides were studied under ozone fumigation. The gaseous ozone fumigation was generated at an ozone rate of 5.5 g.hr^{-1} via an ozone generator using a corona discharger with O_2 input flow rate of 7.5 L.min^{-1} and back pressure of 12 kPa (Changchai et al., 2015). The pesticide coated chili samples were fumigated with ozone gas for 0, 5, 10, 15, 20, 25 and 30 min. The results are shown in Table 18.

Table 18 Pesticide residue concentration of dried chili after ozone fumigation at 0, 5, 10, 15, 20, 25 and 30 minutes.

Fumigation time (min)	**Remaining pesticide concentration ($mg.kg^{-1}$)**					
	Diazion	**Malathion**	**Chlorpyrifos**	**Profenofos**	**Ethion**	**Triazophos**
0	1.87 ± 0.08	1.94 ± 0.13	1.96 ± 0.14	1.95 ± 0.11	2.05 ± 0.02	1.94 ± 0.20
5	1.39 ± 0.02	1.50 ± 0.13	1.67 ± 0.14	1.67 ± 0.15	1.66 ± 0.09	1.62 ± 0.13
10	1.24 ± 0.07	1.28 ± 0.07	1.58 ± 0.06	1.58 ± 0.04	1.32 ± 0.04	1.61 ± 0.05
15	1.09 ± 0.09	1.15 ± 0.03	1.49 ± 0.07	1.47 ± 0.10	1.18 ± 0.06	1.49 ± 0.12
20	0.84 ± 0.04	0.72 ± 0.06	1.08 ± 0.1	1.23 ± 0.04	0.79 ± 0.00	1.13 ± 0.05
25	0.65 ± 0.02	0.72 ± 0.08	0.99 ± 0.04	1.13 ± 0.01	0.73 ± 0.01	1.10 ± 0.03
30	0.57 ± 0.03	0.62 ± 0.03	0.97 ± 0.01	1.07 ± 0.04	0.70 ± 0.08	1.03 ± 0.09

* Data shown represent means of 2 replications with standard deviations.

From Table 18, the initial concentration (C_0) of diazinon, malathion, chlorpyrifos, prefenofos, ethion and triazophos pesticide residue was 1.87, 1.94, 1.96, 1.95, 2.05 and 1.94, respectively. After 30 min of fumigation, concentration of pesticide residues decayed to 0.57, 0.62, 0.97, 1.07 0.70 and 1.03, respectively. According to the maximum concentration of a pesticide residue in International Food Standards recommended by Codex Alimentarius Commission (Codex MRL) value, malathion showed lower final pesticide concentration than Codex MRL which is 1.0 $mg.kg^{-1}$. In contrary, final pesticide concentration after ozone fumigation of diazinon, ethion and triazophos revealed higher Codex MRL number which should not exceed 0.5, 0.3 and 0.1 $mg.kg^{-1}$, respectively (Food and Agriculture Oganization of the United Nations, 2020). The results showed that daizion and malathion revealed high degradation performance while profenofos and triazophos revealed low degradation performance. Typically, the degradation of organic compound by ozone can be divided into 2 types including direct oxidation and indirect oxidation by ·OH formation as follows (Huling and Pivetz, 2006):

Direction Oxidation

$$O_3 + C_2HCl_3 + H_2O \longrightarrow 2CO_2 + 3H^+ + 3Cl^-$$

OH Formation

$$O_3 + H_2O \longrightarrow O_2 + 2{\cdot}OH \text{ (slow)}$$

$$2O_3 + 3H_2O_2 \longrightarrow 4O_2 + 2{\cdot}OH + H_2O \text{ (Fast)}$$

O_3 and ·OH can break down a chemical bonding of pesticide structure into a small chemical structure. A large and complex chemical structure such as profenofos and triazophos will be difficult to degrade (Huling and Pivetz, 2006). Therefore, they revealed low degradation in the experiment.

The pesticide degradation was than calculated in term of C/C_0 in ozone fumigation of dried chili at 0, 5, 10, 15, 20, 25 and 30 minutes, as shown in Table 19 and Figure 18

Table 19 Pesticide degradation of dried chili in term of C/C_0 due to ozone fumigation.

Exposure time (min)	C/C_0					
	Diazion	**Malathion**	**Chlorpyrifos**	**Profenofos**	**Ethion**	**Triazophos**
0	1.00	1.00	1.00	1.00	1.00	1.00
5	0.74	0.77	0.85	0.86	0.81	0.84
10	0.66	0.66	0.80	0.81	0.65	0.83
15	0.58	0.49	0.71	0.75	0.58	0.77
20	0.45	0.37	0.55	0.63	0.39	0.58
25	0.35	0.35	0.50	0.58	0.36	0.57
30	0.31	0.32	0.49	0.55	0.34	0.53

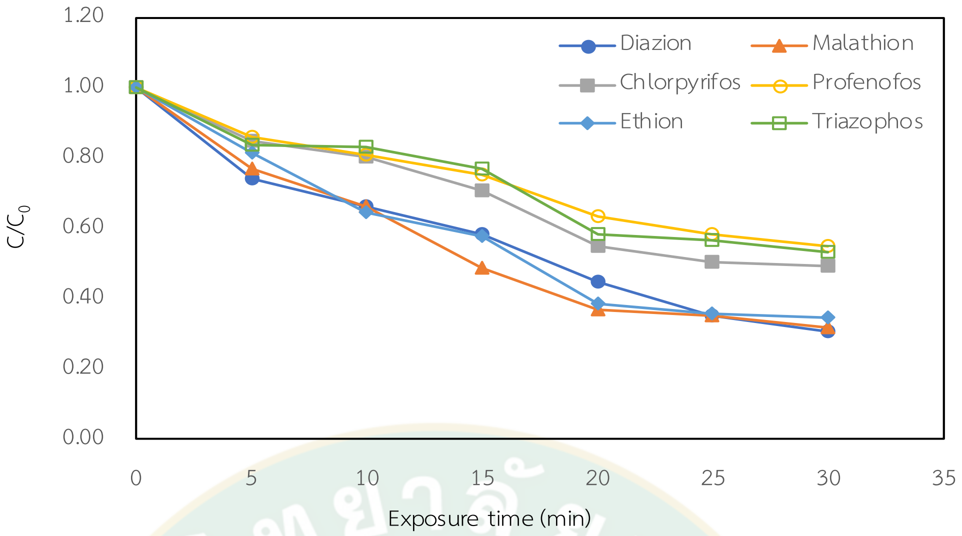


Figure 18 Organophosphate pesticides degradation of dried chili due to ozone fumigation.

The percentages of pesticide residue degradation in dried chili, namely diazinon, malathion, chlorpyrifos, prefenofos, ethion and triazophos after fumigation with ozone gas were 69%, 69%, 51%, 45%, 66% and 47%, respectively, as shown in Figure 19.

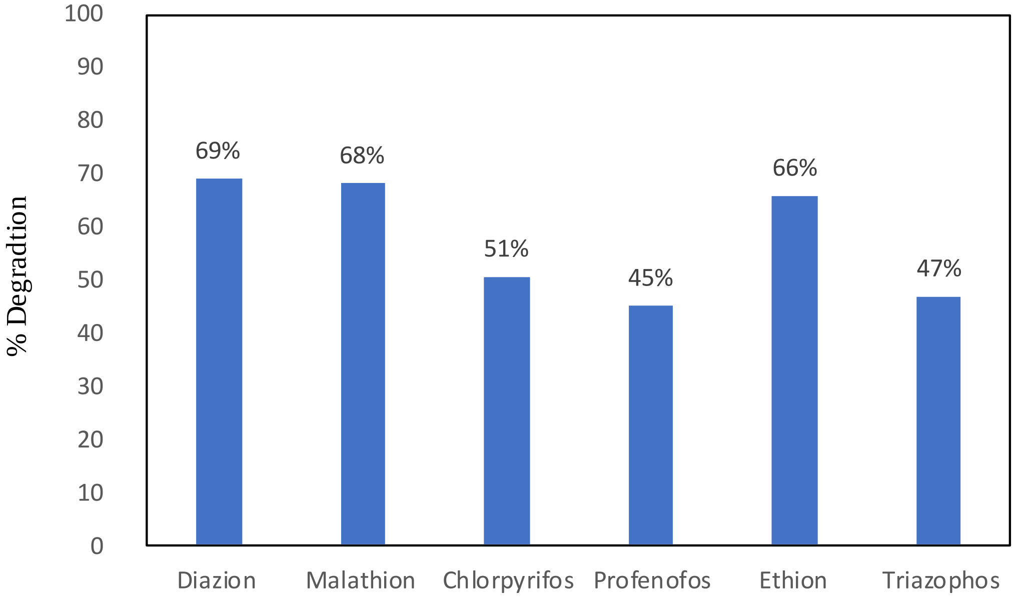


Figure 19 Percentage of pesticide residue degradation after ozone fumigation for 30 minutes.

The reason behind this phenomenon is that ozone is a strong oxidizing agent that can allow pesticide degardation (Ikehata and El-Din, 2006; Ikeura et al., 2011; Tiwari et al., 2010). Therefore, the degradation of pesticide with ozone fumigation exhibited higher efficiency than the degradation without ozone fumigation. The results showed that daizion and malathion revealed high degradation performance of 69 and 68% , respectively, while profenofos and triazophos revealed low degradation performance of 45 and 47%, respectively. This phenomenon resulted from a chemical structure of pesticides. It was found that profenofos and triazophos contain complex structure of six carbon ring called "benzene" which restrict the hydroxyl radical to in the oxidation process. Zuo et al., (2019) also reported the oxidation degradation process of malathion, malaoxon, profenofos, and triazophos. It was also stated that malathion exhibited the greatest degradation activity while triazophos exhibited the lowest degradation activity.

In term of degradation rate constants (k) of organophosphate pesticides, the result is shown in Table 20 and Figure 20.

Table 20 Relationship of remaining pesticide concentration during ozone fumigation process for 30 min in natural logarithm scale.

Exposure time (week)	**Remaining pesticide concentration (ln of mg.kg^{-1})**					
	Diazion	**Malathion**	**Chlorpyrifos**	**Profenofos**	**Ethion**	**Triazophos**
0	0.62	0.66	0.67	0.67	0.72	0.66
5	0.33	0.40	0.51	0.52	0.51	0.49
10	0.21	0.25	0.46	0.46	0.28	0.48
15	0.08	0.14	0.40	0.38	0.17	0.40
20	-0.18	-0.33	0.08	0.21	-0.23	0.12
25	-0.42	-0.32	-0.01	0.13	-0.31	0.10
30	-0.56	-0.48	-0.03	0.07	-0.36	0.03

Degradation kinetics of six organophosphate pesticides by ozone fumigation was considered to be the first order reaction. The degradation rate constants (k) of diazinon, malathion, chlorpyrifos, prefenofos, ethion, and triazophos on non-ozone fumigated chilis were 3.80x10^{-2}, 3.99x10^{-2}, 2.53x10^{-2}, 2.03x10^{-2}, 3.84x10^{-2} and 2.20x10^{-2} mg.kg^{-1}.min^{-1}, respectively. For the degradation half-life period ($t_{1/2}$) of fumigation chili revealed the $t_{1/2}$ for diazinon, malathion, chlorpyrifos, prefenofos, ethion and triazophos of 17.9 ,17.4, 27.4, 34.1, 18.0 and 32.1 minutes, respectively.

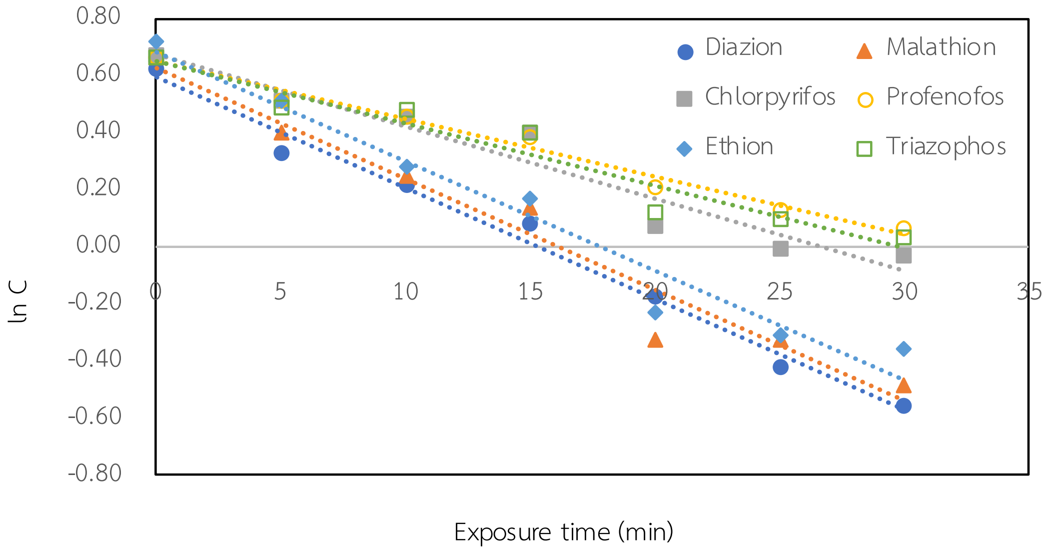


Figure 20 First-order kinetics plot of the organophosphate pesticides degradation with ozone fumigation 30 minutes.

Table 21 shows the kinetics parameters of the organophosphate pesticides degradation during storage at 25°C and with ozone fumigation. To compare both degradation, the degradation rate constant (k) and degradation half-life period ($t_{1/2}$) were approximately 10,000 fold different in the order of magnitude. Both non-ozonated and ozonated chili exhibited similar trend of pesticide residue degradation. The degradation on ozonated chili exhibited higher degradation rate constant (k) than that of the non-ozonated chili. The higher degradation rate constant reflected the shorter time for pesticide residue to decay. In consequence, the half-life period ($t_{1/2}$) of pesticide on ozonated chili was much shorter than that in non-ozonated chili. Our results corresponded well with the previous work by Bourgin et al. (2013) who reported that the degradation of pesticide on moisten wheat seed by ozonation fumigation for

96 min was the first-order reaction with degradation percentage of 99% for midacloprid and 90% for bitertanol.

Table 21 Kinetics parameters of the organophosphate pesticides degradation during storage at 25°C with and without ozone fumigation

Pesticide	Non-ozone fumigation			Ozone fumigation			Half-life time difference (%)
	k ($mg.kg^{-1}.min^{-1}$)	R^2	$t_{1/2}$ (day)	k ($mg.kg^{-1}.min^{-1}$)	R^2	$t_{1/2}$ (min)	
Daizion	7.00×10^{-6}	0.94	68.8	3.80×10^{-2}	0.99	17.9	99.9%
Malathion	7.22×10^{-6}	0.92	66.6	3.99×10^{-2}	0.95	17.4	99.9%
Chlorpyrifos	6.35×10^{-6}	0.98	75.7	2.53×10^{-2}	0.94	27.4	99.9%
Profenofos	6.54×10^{-6}	0.96	73.5	2.03×10^{-2}	0.98	34.1	99.9%
Ethion	3.98×10^{-6}	0.93	120.9	3.84×10^{-2}	0.96	18.0	99.9%
Triazophos	6.00×10^{-6}	0.88	80.2	2.20×10^{-2}	0.94	32.1	99.9%

It is noted that the *k* value, which was a slope of first-order kinetic equation according to Equation 2, exhibited a proportional relationship with reaction rate. As the *k* value increased, the degradation rate of pesticide increased. On the other hand, the *k* value exhibited an inverse relationship to $t_{1/2}$ value. The shorter $t_{1/2}$ period, the faster the pesticide residue to degrade. Hence, the effective process to degrade pesticide residue on dried chili should possess high value of *k* and low value of $t_{1/2}$, which was achieved by ozone gas fumigation in this work.

4.1.3 Physical properties of ozonated chili

Water activity of dried chili after ozone fumigation was found to be in the range of 0.62–0.69, as shown in Table 22. The ozone fumigation did not significantly affect ($p \geq 0.05$) the water activity of dried chili compared to that of control. Since water activity is an indicator for free water content, the low water activity also indicates the low free water existing inside dried chili. Due to low free water content in dried chili, it is possible that the oxidation reaction occurred during ozone fumigation was not dominated by chemical reaction between ozone and free water. However, the oxidation reaction taken place during ozone fumigation of dried chili was likely to be dominated by chemical reaction between ozone and pesticides which was coated on the outer skin of the chili. As a result, water activity of dried chili did not significantly change ($p \geq 0.05$) after ozone fumigation.

Color of dried chili after ozone fumigation for 5, 10, 15, 20, 25 and 30 min was indicated by lightness (L*), redness (a*) and yellowness (b*). It was found that L* a* and b* values were not significantly different ($p \geq 0.05$), meaning that ozone fumigation did not significantly affect ($p \geq 0.05$) the color of dried chili. This was confirmed by the non-significant difference ($p \geq 0.05$) of the total color difference ΔE as well. Our results in this study corresponded to the previous work reported by Changchai et al. (2015) who reported that the color of fresh chili fruit was not affected by ozone treatment during disinfestation of fruit fly larvae in fresh chili using ozone fumigation. Normally, ozone has a color bleaching effect (increasing lightness, L*) (Aday and Caner, 2014), the fresh produces which contains high amount of free water content is more susceptible to the bleaching of color than that of dried products. In this work, the dried chili contains low amount of free water content as indicated in low water activity, it limits chemical reaction that would cause bleaching effect. Therefore, lightness of dried chili in this work remains unchanged.

Table 22 Water activity and color of dried chili after ozone fumigation.

Exposure time (min)	Water activity $^{(n.s)}$ a_w	Color qualities $^{(n.s)}$			
		L*	a*	b*	ΔE
0	0.66± 0.02	35.22 ± 4.40	26.63 ± 5.01	13.61 ± 5.07	-
5	0.63 ± 0.01	29.60 ± 0.92	29.89 ± 1.30	16.24 ± 0.31	7.05 ± 1.33
10	0.69 ± 0.00	32.20 ± 3.84	25.91 ± 2.74	12.77 ± 1.77	3.95 ± 4.18
15	0.67 ± 0.01	32.01 ± 1.52	24.33 ± 4.07	11.90 ± 3.91	6.21 ± 2.05
20	0.66 ± 0.01	29.17 ± 5.13	26.69 ± 5.94	14.46 ± 2.58	8.58 ± 3.73
25	0.62 ± 0.05	29.13± 1.98	26.07 ± 4.41	12.31 ± 3.32	7.83 ± 0.60
30	0.65 ± 0.02	30.93 ± 3.49	24.43 ± 4.14	11.25 ± 2.42	8.05 ± 1.39

**n.s. = not significantly different ($p < 0.05$).

***Exposure time at 0 min refers to non-ozone fumigation.

****Data shown represent means of 3 replications with standard deviations.

4.1.4 Analysis of capsaicin

Table 23 indicates that the capsaicin content of dried chili tended to decrease with increasing exposure time but was not statistically different ($p \geq 0.05$). After ozone fumigation, the dried chili which contained an initial capsaicin content of 3205 mg.kg^{-1} decreased to 3095, 3080, 3035, 3030, 2833 and 2832 mg.kg^{-1} on increasing fumigation time of 5 min increment. From the previous report, capsaicin was found mainly in ovary part of chili (Supalkova et al., 2007). Thus, it was possible that ozone fumigation was not long enough to allow ozone gas to penetrate the chili ovary, which resulted in non-significant difference in capsaicin content due to ozone exposure time within 30 min.

Table 23 Capsaicin content of dried chili after ozone fumigation

Exposure time (min)	Capsaicin content $^{(n.s)}$ (mg.kg^{-1})
0	3,205 ± 317
5	3,095 ± 182
10	3,080 ± 293
15	3,035 ± 148
20	3,030 ± 154
25	2,833 ± 476
30	2,832 ± 218

*n.s. = not significantly different ($p < 0.05$).

**Data shown represent means of 3 replication with standard deviations.

As ozone is an strong oxidizing agent, it may affect the quality of food such as color loss and degradation of phenolic compound, antioxidant compound (Karaca and Velioglu, 2014). Therefore, exposure time of ozone fumigation is an important parameter that should be concerned to avoid qualities change. Our results showed that the fumigation time of 30 min can be used to degrade organophosphate pesticide without any significant change in chili qualities, This corresponds to the results from previous reports that ozone was used to reduce pesticide in lychee effectively without any weight loss and soluble solid change (Whangchai et al., 2011). Thus, it is suggested that if the ozone fumigation process to be further developed, the dried chili should be exposed to ozone gas no longer than 30 min to maintain its qualities, and capsaicin content.

4.1.5 Analysis of total phenolic content (TPC) and free radicals scavenging activity

The TPC and free radicals scavenging activity representing the natural chemical property of dried chili are shown in Table 24.

Table 24 Total phenolic content and free radical scavenging activity of chili sample with ozone fumigation for 30 min.

Exposure time (min)	Total phenolic content (mgGAE. 100 g^{-1})	Free radical scavenging activity (mgTEAE. 100 g^{-1})$^{n.s.}$
0	150.27^{a} ± 8.62	51.01 ± 5.57
5	145.28^{a} ± 2.98	43.94 ± 0.61
10	147.81^{a} ± 6.86	51.69 ± 3.68
15	150.93^{a} ± 6.28	44.30 ± 0.81
20	150.83^{a} ± 5.01	51.73 ± 0.85
25	145.53^{a} ±9.77	44.33 ± 5.34
30	130.00^{b} ± 5.64	49.10 ± 1.22

*n.s. = not significantly different ($p \geq 0.05$).

**Values followed by the different letter within the same row are significantly different from each other ($p < 0.05$).

***Data shown represent means of 3 replication with standard deviations.

The TPC tended to decrease slightly due to fumigation time at 0, 5, 10, 15, 20 and 25 min but was not significantly different ($p \geq 0.05$). However, after fumigation for 30 min, the TPC was significantly different ($p < 0.05$) from the others. This phenomenon occurred due to reaction by ozone and free radical caused by ozone (·OH) that are strong oxidizing agents. Therefore, long duration of ozone fumigation could result in the degradation of phenolic content in dried chili (Misra et al., 2015; Sarangapani et al., 2017). For the free radical scavenging activity, there was no significantly different on fumigation 0 to 30 min, as shown in Table 24. The results from this experiment was corresponded to the previous reports (Alwi, 2017; Torres et al., 2011) who found that total phenolic compound reduced by the increasing of ozone concentration or time of fumigation. To prevent the reduction TPC and other antioxidant compounds in dried chili as well as to maintain chili physical properties, the experimental procedure in part 2 was designed by reducing fumigation time from 30 to 20 min.

4.1.6 Scanning electron microscopy (SEM) analysis

SEM image of chili surface morphology without ozone fumigation was compared that with ozone fumigation for 30 min, as shown in Figure 21. It was found that ozone affected surface morphology of chili. An increase in roughness structure of chili surface was observed after ozone treatment. This phenomena can not be clearly explained but it is possible that the ozone fumigation at high concentration may have oxidative reaction with some substance at surface causing the distort morphological changes as a rougher or corrosive surface of the chili (Alwi, 2017; O'Donnell et al., 2012)

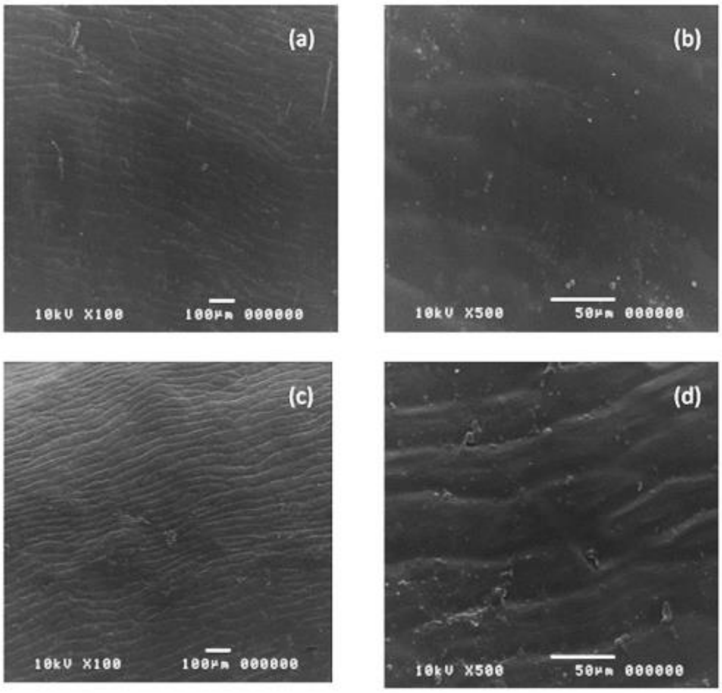


Figure 21 SEM image of chili surface : (a, b) without ozone fumigation and (c, d) with ozone fumigation for 30 min

4. 2 Parameters affecting ozone fumigation using vertical forced- air (VFA) technique

4.2.1 Study of pressure drop

In the VFA circulation system, the baskets of chili were stacked in vertical orientation. This caused the pressure drop across the stack or layer of the basket. Pressure drop is an important parameter indicating the gas distribution in chamber containing died chili basket. Ideally the uniform gas distribution can result in good ozone penetration to the chili inside the basket. There are several parameters affecting pressures drop in the chamber namely, air flow rate, air velocity, cross-sectional area of basket and chili load. Therefore, relationship between forced– air circulation parameters and pressure drop value is determined to evaluate dimensional analysis using Buckingham's π theorem on dry chili's basket when apply vertical forced-air ozone fumigation.

4.2.1.1 Effect of air flow rate and air velocity on air distribution in fumigation chamber

In the experiment the air flow rate was regulated by adjusting the voltage of circulating fan. The input voltage of circulating fan affected air flow rate in VFA circulation system which is presented in Table 25.

Table 25 Air flow rate of VFA system at various fan input voltage.

Input voltage (V)	Cross-sectional of basket (m^2)	Average air velocity through basket ($m.s^{-1}$)	Air Flow rate ($m^3.s^{-1}$)
60	0.105	0.90 ± 0.53	0.09 ± 0.06
90	0.105	1.37 ± 0.70	0.14 ± 0.07
120	0.105	1.93 ± 1.08	0.20 ± 0.11
150	0.105	2.49 ± 1.33	0.26 ± 0.14
180	0.105	3.02 ± 1.41	0.32 ± 0.15
210	0.105	3.09 ± 1.23	0.32 ± 0.13

*Data shown represent means of 9 replications with standard deviations.

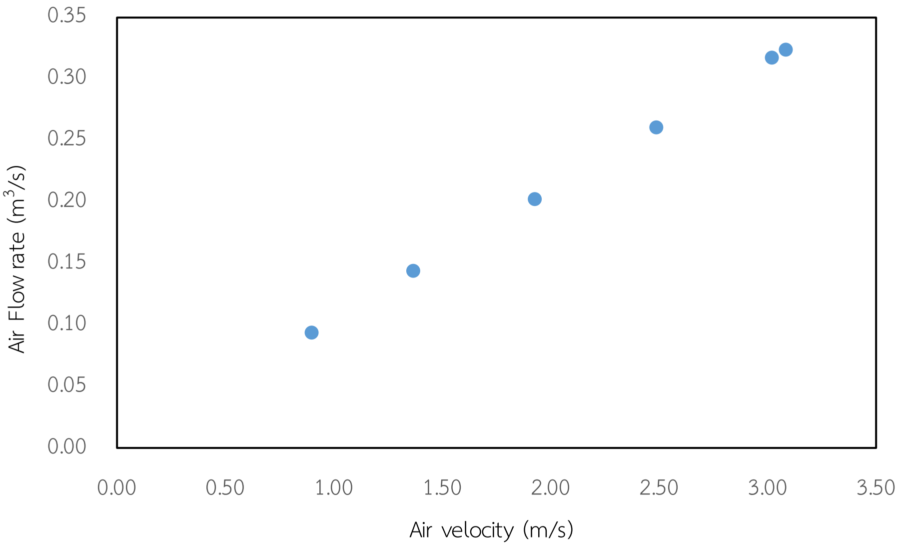


Figure 22 Relationship between air flow rate and air velocity through the basket

Figure 22 shows that air flow rate increased linearly from 0.09 to 0.32 $m^3.s^{-1}$ with increasing air velocity from 0.09 to 3.09 $m.s^{-1}$, respectively. Then, various air flow rates of 0.09, 0.14, 0.20, 0.26, and 0.32 $m^3.s^{-1}$ were used in the further study of pressure drop in fumigation chamber.

4.2.1.2 Effect of air flow rate on pressure drop across chili baskets

Pressure drop across chili basket stacks with different dried chili load stacking of 1, 2, 3, 4, and 5 kg (1kg/basket) was studied at various air flow rate of 0.09, 0.14, 0.20, 0.26, and 0.32 $m^3.s^{-1}$. The results shown in table 26 and Figure 23 indicated that an increase in air flow rate and sample load stacking caused in an increase in pressure drop. The results corresponded with the Bernoulli effect that pressure drop depends on flow rate and height of stack. Moreover, the acceleration of the air in the gap causes a drop in pressure (Waltham et al., 2003). The results were corresponded well with the previous reports (Delele et al., 2008; Vigneault and Goyette, 2003). Pressure drop was found to be a key parameter that affect to penetration of gas.

Table 26 Pressure drop across basket stack at various air flow rate

Air Flow rate	Pressure drop (hPa)				
Q ($m^3.s^{-1}$)	1	2	3	4	5
0.09	0.17 ± 0.02	0.22 ± 0.02	0.26 ± 0.01	0.28 ± 0.03	0.30 ± 0.00
0.14	0.54 ± 0.01	0.58 ± 0.01	0.61 ± 0.02	0.73 ± 0.02	0.81 ± 0.04
0.20	0.86 ± 0.01	0.91 ± 0.01	0.94 ± 0.03	1.16 ± 0.01	1.30 ± 0.05
0.26	1.12 ± 0.01	1.22 ± 0.01	1.34 ± 0.00	1.52 ± 0.03	1.74 ± 0.08
0.32	1.32 ± 0.02	1.49 ± 0.04	1.62 ± 0.01	1.87 ± 0.01	2.08 ± 0.13

*Data shown represent means of 3 replications with standard deviations.

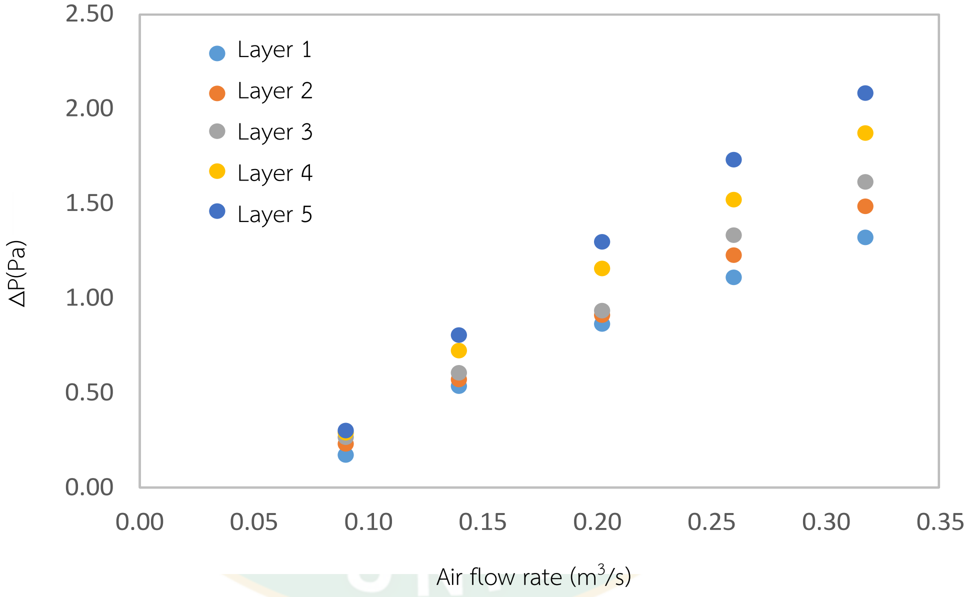


Figure 23 Effect of air flow rate on pressure drop in between chili basket layers

4.2.1.3 Dimensional analysis

Dimensional analysis was used as a mathematical model to characterize the ozone distribution in fumigation chamber by VFA circulation using buckingham Pi theorem. The Buckingham Pi theorem states that " the number of dimensionless and independent quantities required to express a relationship among variables in any phenomenon is equal to the number of quantities involved minus the number of dimensions in which those quantities may be measured" (Reese et al., 1977). For the ozone VFA fumigation system, the variables and their corresponding dimensions used in model development given as follows:

	ΔP	ρ	C/C0	μ	v_s	A	ε_v	L
M	1	1	0	1	0	0	0	0
L	-1	-3	0	-1	1	2	0	1
T	-2	0	0	-1	-1	0	0	0

Therefore, number of π group is N; therefore, π = 8-3 = 5. The mathematical expression of pressure drop between the dependent variable is as shown in Equation 18.

$$\Delta P = \int\left(\rho, \frac{C}{\square_0}, \mu, \nu_\square, A, \varepsilon_\square, L\right) \qquad (18)$$

The dimensionless Pi's terms obtained are shown in Equation 21 – 25

$$\pi_1 = \frac{\Delta P}{\rho v^2} \quad \text{Euler number, Eu} \qquad (21)$$

$$\pi_2 = \frac{\rho v L}{\mu} \quad \text{Reynolds number, Re} \qquad (22)$$

$$\pi_3 = \frac{A}{L^2} \qquad (23)$$

$$\pi_4 = \frac{C}{C_0} \qquad (24)$$

$$\pi_5 = \varepsilon \qquad (25)$$

4.2.1.3 Correlation between dimensionless numbers (Eu number, Re number, A/L^2) and pressure drop

Superficial velocity of air flow through baskets in the top of each layers was measured and calculated to determine correlation between dimensionless numbers (Eu number, Re number, A/L^2 and D_H/L) and pressure drop (ΔP) as shown in

Table 27. The air was forced through the 5 baskets with circulating fan using power in the range of 480, 668, 816, 950 and 1,051 watts. Dried chili was loaded into baskets varied from 1 to 5 kg. Each layer of basket contained 1 kg of dried chili. Air velocity was averaged from 9 points measurements using hot wire air velocity meter (TENMARS, TM-4002, Taiwan). The Eu number was calculated according to Equation 21. In this experimental, the porosity of dried chili was used to calculate the Re number by Equation 26 which was modified from Equation 22 as a pack bed model. The result is shown in Table 28.

$$\mathrm{Re} = \frac{\rho v_s d}{\mu} \frac{1}{1-\varepsilon_v} \tag{26}$$

Where: ρ = Density of air (kg.m^{-3}) is 1.22 kg.m^{-3}

μ = Viscosity of air (Kg.m^{-1}s^{-1}) is 1.81×10^{-5} kg.m^{-1}.s^{-1}

v_s = Superficial velocity (m.s^{-1})

ε_v = 0.4 (measured by pycnometer)

d = 0.07 m (diameter of dried chili)

Table 27 Average superficial of air velocity through baskets layers at various flow rates

Air Flow rate (m^3.s^{-1})	**Average superficial of air velocity (m.s^{-1})**				
	Sample loads (kg)				
	1	**2**	**3**	**4**	**5**
0.90	0.68	0.70	0.71	0.78	0.79
1.37	1.31	1.37	1.46	1.43	1.43
1.93	1.94	1.91	2.00	1.92	1.61
2.49	2.53	2.42	2.54	2.38	2.16
3.02	2.93	2.88	2.61	2.91	2.62

*Data shown represent means of 9 replication with standard deviations.

Table 28 Relationship of Re and Eu number of each layer at various A/L^2

Air flow rate ($m^3.s^{-1}$)	Re number at various A/L^2				
	6.23	1.56	0.69	0.39	0.25
0.90	2,138.93	2,207.08	2,229.80	2,446.49	2,483.19
1.37	4,132.82	4,302.33	4,578.43	4,487.56	4,498.05
1.93	6,109.24	6,018.37	6,283.99	6,037.59	5,057.25
2.49	7,949.35	7,602.47	8,000.02	7,475.78	6,804.74
3.02	9,204.05	9,057.26	8,194.00	9,151.62	8,232.44
Air flow rate ($m^3.s^{-1}$)	Eu number at various A/L^2				
	6.23	1.56	0.69	0.39	0.25
0.90	0.30	0.37	0.42	0.38	0.39
1.37	0.25	0.25	0.23	0.29	0.71
1.93	0.19	0.20	0.19	0.26	0.41
2.49	0.14	0.17	0.17	0.22	0.30
3.02	0.13	0.15	0.20	0.18	0.25

Re numbers and Eu numbers are dimensionless numbers that present air flow characteristic. Therefore, velocity of air flow through the basket layers was measured in order to determine correlation between dimensionless numbers (Eu numbers, Re numbers, A/L^2) and pressure drop (ΔP). From this experiment, Eu was plotted with A/L^2. It was found that there is no mathematical relationship in term of Eu numbers as shown in Figure 25. On the other hand, Re numbers revealed a significant correlationship with A/L^2 as shown in Figure 24. Consequently, Re numbers could be used as dimensionless numbers to represent size a height of basket layers in order to apply in scaling-up of the fumigation system.

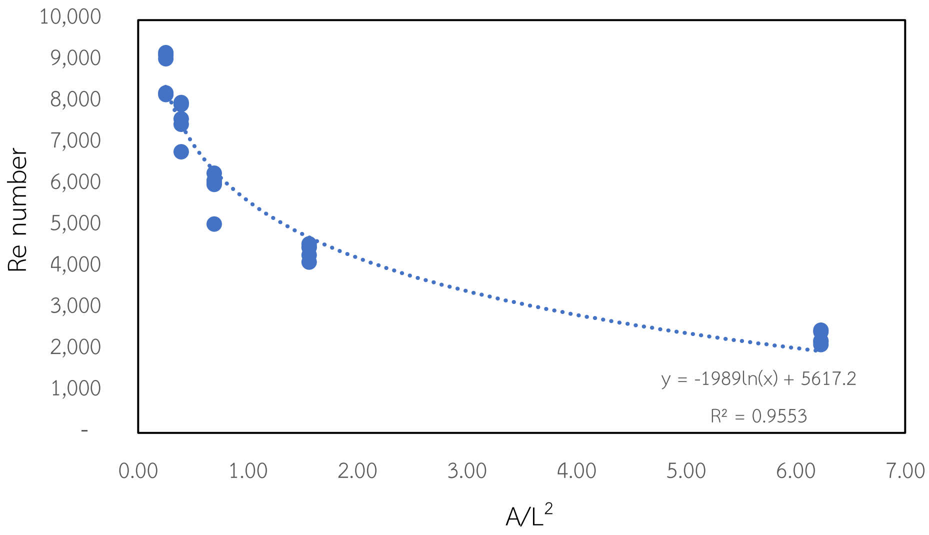


Figure 24 The correlation between Re number and A/L^2

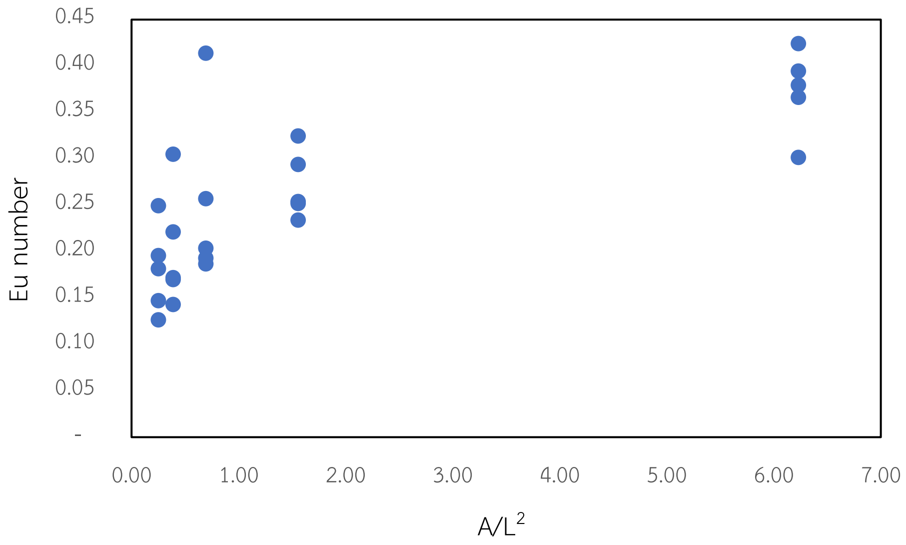


Figure 25 The correlation between Eu number and A/L^2

Figure 24 shows that the Re number declined sharply with increasing A/L^2 from 0.25 to 1.56, and declined gradually with increasing A/L^2 of 1.56 to 6.23. The equation from this relationship was expressed by exponential decay model as: $y = -1989\ln(x) + 5617$ with R^2 0.9553.

To simplify the utilization of mathematical model, relationship between Re numbers and pressure drop was further determined. The results showed that the Re numbers correlated with pressure drop revealed correlation as shown in Figure 26. It was found that pressure drop increased with increasing of Re number because of increased air flow rate inside the OVFA chamber. Moreover, pressure drop increased with the number of baskets stacking within the fumigation chamber because the baskets stacking containing dried chili obstructed the air flow throughout the chamber. The mathematical correlation was found to be $y = 0.0002x – 0.1669$ with $R^2 = 0.7913$.

The Re number in pack bed model can be divided into 2 types of flow including laminar flow (Re<2,000) and turbulent flow (Re ≥ 2,000) (Ellenberger, 2014). In this experiment, The Re number was in the range of 2,138.93 - 8,232.44. Therefore, the OVFA flow in this experiment was considered as the turbulent flow.

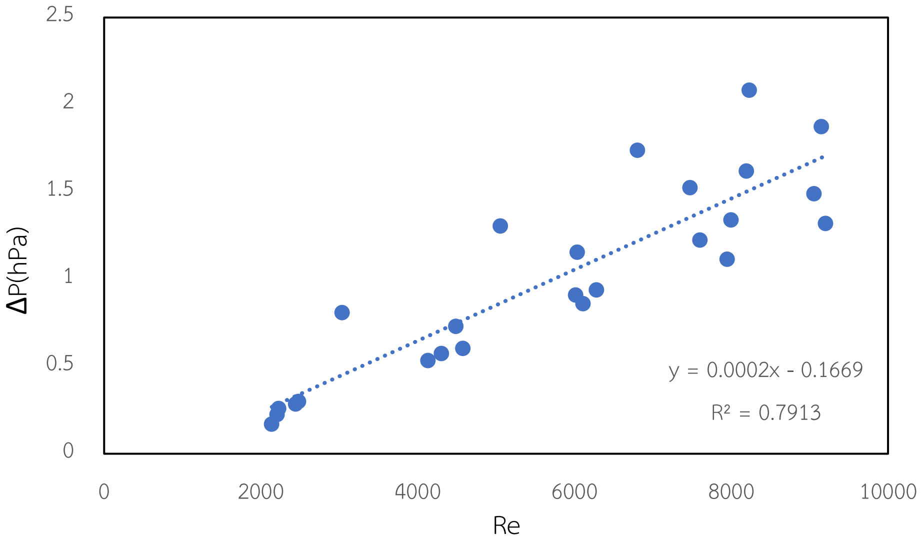


Figure 26 Relationship of Re numbers and pressure drop

4.2.2 Pesticide residue degradation in dried chili treated by OVFA fumigation

Gaseous ozone with average initial concentration of 7,500 ppm was filled into fumigation chamber of dried chili samples for 20 min. Air flow rate of forced-air circulation system was generally correlates with pressure drop. We found that pressure drop increased with increasing air flow rate and also with increasing stack height. Pressure drop is also a function of air density, air viscosity, air velocity and flow area cross-section area as well.

To proof the uniformity of ozone distribution due to the flow design, the pesticide residue after ozone treatment was used as an indicator. One kg of dried chili with contaminated pesticide with initial concentration of 2.44 $mg.kg^{-1}$ was packed per one basket and fumigated for 20 min by OVFA circulation an average ozone concentration of 7,500 ppm and air flow rates at 0.09, 0.20 and 0.32 $m^3.s^{-1}$. The result is shown in Table 29. It was found that degradation percentage increased with increasing air flow rate from 0.90-0.32 $m^3.s^{-1}$ and increasing stack height from 1-5 baskets. The reason is that an increase in number of stacking baskets and the Re number enhanced in air/ozone contact of contaminated chili. Therefore, rapid degradation of pesticide residue took place effectively. However, as the number of stacking increased, SD value became wider which implied a less-uniformity of degradation among difference baskets stack. For example, at air flow rate of 0.90 $m^3.s^{-1}$, the SD in table 29 increased from 0.54 to 3.02% with increasing stack number from 3 to 5 baskets, respectively. Moreover, when considering effect of air flow rate to the degradation uniformity, the SD at 5 baskets stacking increased from 3.02 to 6.6% with increasing air flow rate from 0.09 to 0.32 $m^3.s^{-1}$, respectively. Therefore, it can be stated that the uniformity of pesticide degradation in low air flow rate and small basket stacking was found to be more uniform than those at higher air flow rate and more basket stacking. However, in our research, the OVFA system can degrade pesticide residue in a range from 49-77% after fumigation for 20 min. This seems to be satisfactorily acceptable and evidently proofed the flow characteristic of ozone to be analogy to the ambient air flow using the same dimensional analysis.

Table 29 Percentage of chlorpyrifos pesticide residues in Force air circulation by gaseous ozone for 20 minutes.

Air flow rate ($m^3.s^{-1}$)	Load (kg)	Layer	Pesticide residue ($mg.kg^{-1}$)	Degradation (%)	Average	SD	Re number
0.09	1	1	0.58	71%	71%		2,138.93
	3	1	1.11	54%	55%	0.54%	2,229.80
		2	1.08	56%			
		3	1.10	55%			
	5	1	0.88	64%	63%	3.02%	2,483.19
		2	1.04	58%			
		3	0.86	65%			
		4	0.83	66%			
		5	0.96	61%			
0.20	1	1	0.75	66%	66%		6,109.24
	3	1	1.02	58%	55%	2.82%	6,283.99
		2	1.19	51%			
		3	1.09	55%			
	5	1	1.10	55%	66%	8.07%	5,057.25
		2	1.00	59%			
		3	0.75	69%			
		4	0.74	70%			
		5	0.55	77%			
0.32	1	1	0.84	66%	66%		9,204.05
	3	1	1.06	57%	56%	2.58%	8,194.00
		2	1.00	59%			
		3	1.15	53%			
	5	1	1.24	49%	56%	6.60%	8,232.44
		2	1.11	55%			
		3	0.78	68%			
		4	1.20	51%			
		5	1.08	56%			

From the results of the experiment, it was found that every point of the experiment was able to reduce the amount of pesticide residue by 49-77% within a period of 20 minutes. The distribution of the pesticide degradation at air flow rate of $0.09 m^3.s^{-1}$ exhibited the lowest SD when compared to the flow rates of 0.20 and 0.32 $m^3.s^{-1}$. The high air flow rate and high air velocity generated different ozone penetration capability among different position of dried chili in the baskets. However, using the low air flow rate caused better decomposition of pesticides and better uniformity of ozone distribution in the fumigation chamber.

Figure 27 exhibits the plot of acceptance area that can be used for the OVFA process design. The acceptance area as shown in Figure 27 was to ensure that pesticide degradation could be achieved in good uniformity of ozone distribution with SD<5% and pesticide degradation more than 50%. To simplify a further application of pesticides degradation using OVFA, the relationship of pesticide degradation, C/C_0 and pressure drop efficiency was determined, as shown in Figure 28.

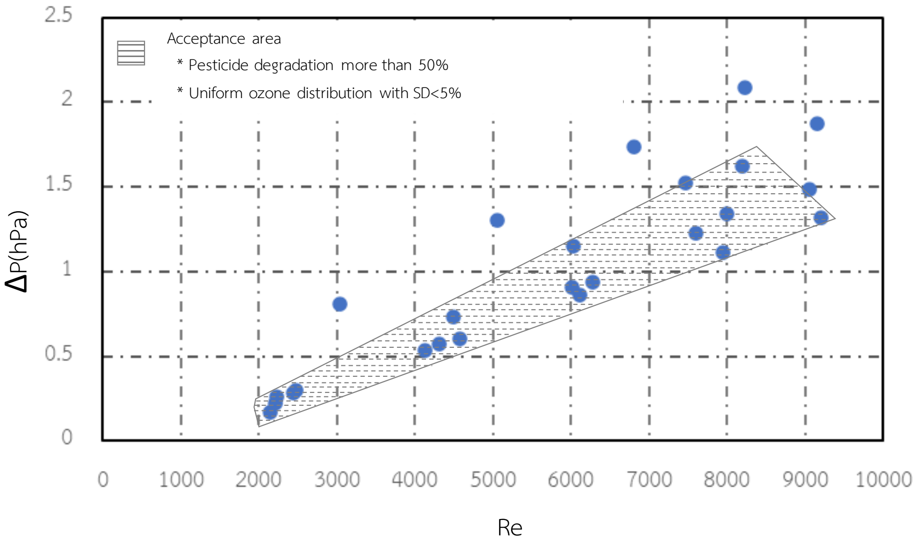


Figure 27 Acceptance area to ensure that pesticide degradation was greater than 50% and uniform ozone distribution with SD<5%

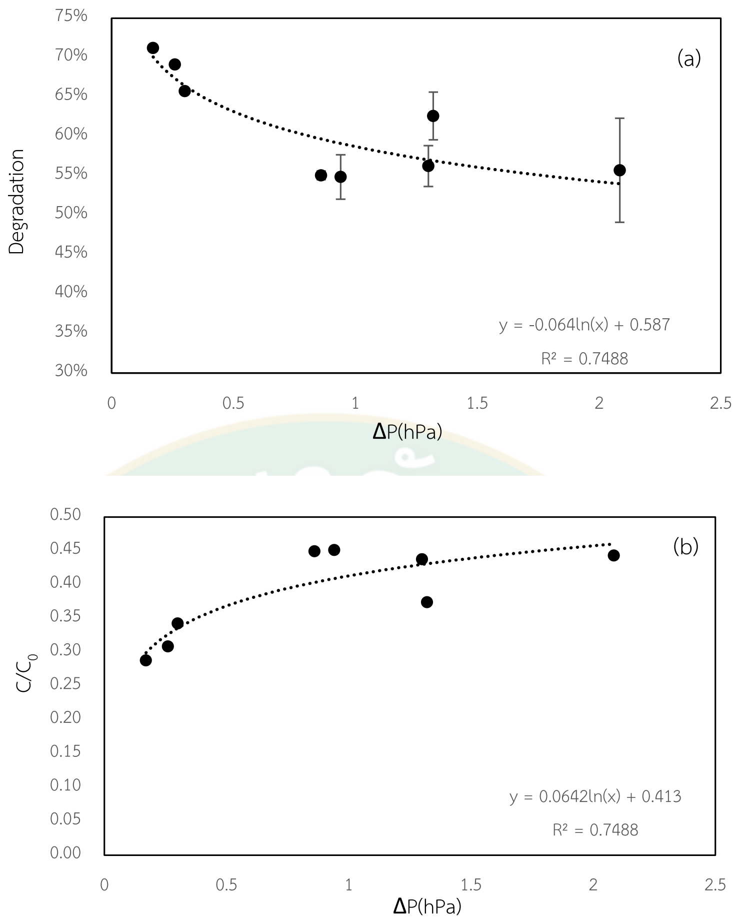


Figure 28 Effect of pressure drop on (a) degradation percentage and (b) C/C_0 of chlorpyrifos in forced-air circulation system

4.2.3 Conceptual design for commercial scale application

To design OVFA system for commercial scale application with large capacity, the A/L^2 is taken into account for the calculation of the Re number, pressure drop, and degradation percentage, respectively.

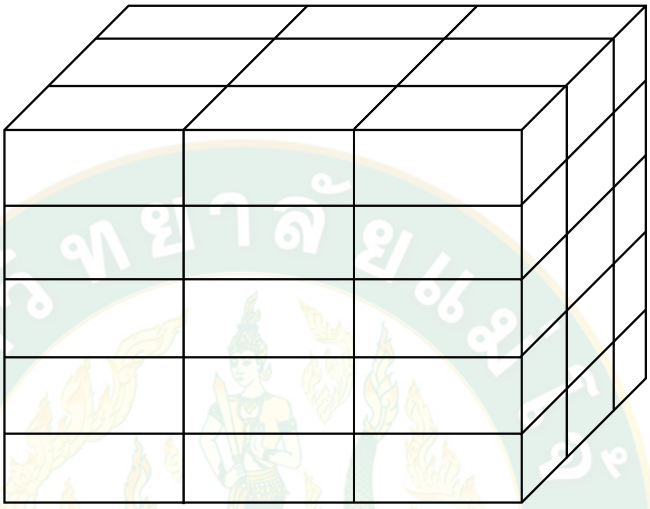


Figure 29 Example of dried chili baskets arrangement in the commercial sacle OVFA system

To provide better understanding we propose the example of enlarge capacity for OVFA at industrial scale. In Figure 29, dried chili baskets were arranged in OVFA system for pesticide degradation with 45 baskets (0.27 x 0.39 x 0.13 m^3) in 3 x 3 x 5 (row x column x stack) baskets to obtained system dimension of 0.81 x 1.17 x 0.65 m^3. To a calculate the design of system, the appropriate pressure number in the pesticide degradation, it is calculated as follows:

Determination of A/L^2

$$A = (0.39*3)*(0.27*3)$$
$$= 0.9477\ m^2$$
$$L^2 = ((0.13*5)^2)$$
$$= 0.4225\ m^2$$

Thus
$$A/L^2 = (0.9477/0.4225)$$
$$= 2.24$$

Determination of Re number

$$\text{Re} = -1989 \ln (A/L^2) + 5617$$

$$= 4013.12$$

Determination of ΔP

$$\Delta P = 0.00008\ \text{Re} - 0.1669$$

$$= 0.00008\,(4013.12) - 0.1669$$

$$= 0.63$$

Determination of degradation percentage

$$\%\ \text{degradation} = -\,0.064 \ln (\Delta P) + 0.587$$

$$= -\,0.064 \ln (0.62) + 0.587$$

$$= 62\ \%$$

Therefore, in the OVFA system for pesticide degradation with total number of 45 baskets and total dimension of 0.81 x 1.17 x 0.65 m^3, as shown in Figure 29, the appropriate circulating fan should overcome the pressure drop of 0.63 hPa to degrade pesticide residues approximately 62% within 20 min.

4.2.4 Operation cost of ozone fumigation with forced-air circulation system

Table 30 shows cost of OVFA system at O_2 gas input flow rate of 7.5 $L.min^{-1}$ for 20 min by comparing between the non-circulation and forced-air circulation at the air flow rate of 0.09, 0.20 and 0.30 $m^3.s^{-1}$. In both cases, same oxygen rate was used which was 8.025 THB. The electricity cost for forced-air circulation technique at the air flow rate of 0.09, 0.20 and 0.30 $m^3.s^{-1}$ was 0.58, 0.99 and 1.27 THB, respectively. The major cost electricity is from the circulating fan and the ozone generation system. Electricity cost for non-circulation system was 0.25 THB which costed only form the ozone generator system. The results showed that operating cost for pesticide degradation increased with increasing of forced-air flow rate. However, pesticide degradation at air flow rate of 0.09 $m^3.s^{-1}$ yielded the highest degradation percentage of 71% while the high air flow rate at 0.32 $m^3.s^{-1}$ yielded only 56%. Therefore, operation cost per 1% pesticide degradation was further calculated. It was found that operation cost for the reduction of 1% of pesticide under non-circulation and forced-air circulation with air flow rate of 0.09, 0.20 and 0.30 $m^3.s^{-1}$ was 0.184, 0.121, 0.131 and 0.135 THB, respectively. Hence, it confirmed that forced-air circulation with air flow rate of 0.09 $m^3.s^{-1}$ was the most prominent condition in this research for the pesticide degradation by ozone fumigation process because it gave the best operating cost per percentage of reduction of chlorpyrifos pesticide. The novel ozone fumigation with OVFA system saved operation cost per pesticide reduction percentage by 34% compared to non-VFA system.

Table 29 Operation cost per 1% reduction of pesticide by ozone fumigation in 1 kg dried chili with forced-air circulation system at 20 minutes.

Air flow rate of the OVFA system ($m^3.s^{-1}$)	**Electricity cost (THB)**	**Oxygen gas cost (THB)**	**Degradation (%)**	**Operation cost per 1% reduction of pesticide (THB)**	**Percentage of cost saving (%)**
0	0.25	8.025	45	0.184	Base line
0.09	0.58	8.025	71	0.121	+34.09
0.2	0.99	8.025	66	0.131	+28.95
0.32	1.27	8.025	66	0.135	+26.74

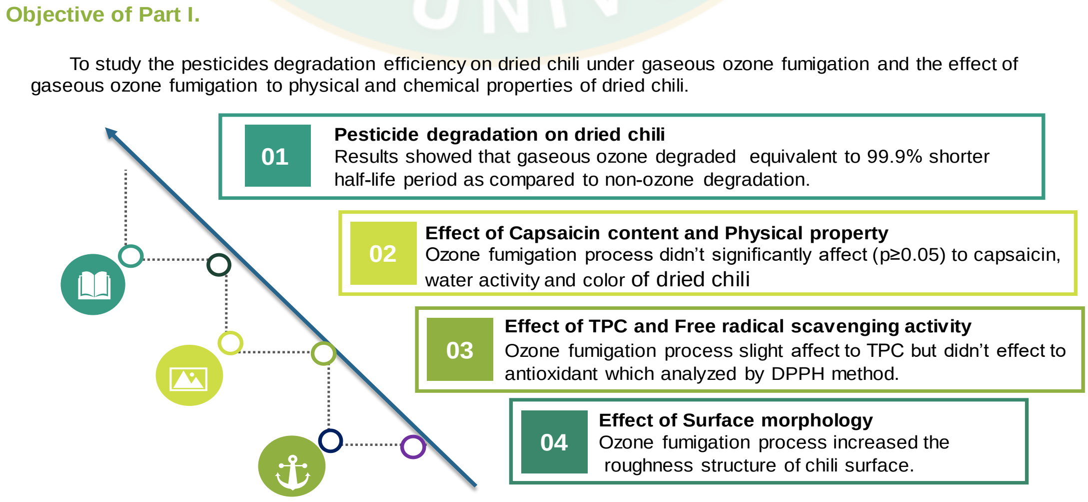
CHAPTER 5

CONCLUSION

This dissertation presents the develop of ozone fumigation process to degrade the pesticide residue on dried chili.

In the first part, the gaseous ozone fumigation in pressurize polycarbonate tank was successfully degraded 6 organophosphate pesticides, namely diazinon, malathion, chlorpyrifos, prefenofos, ethion and triazophos where the degradation kinetics of organophosphate pesticides exhibited the first- order reaction. Gaseous ozone degraded diazinon, malathion, chlorpyrifos, prefenofos, ethion and triazophos with the $t_{1/2}$ values of 17.9 ,17.4, 27.4, 34.1, 18.0 and 32.1 mins, respectively, where dried chili without ozone fumigation had $t_{1/2}$ values of 68.8 ,66.6 75.7, 73.5, 120.9 and 80.2 days, respectively. The $t_{1/2}$ value of ozonated dried chili was 99.9% shorter than that of the non ozoneted.

Ozone fumigation did not significantly affect ($p \geq 0.05$) water activity, color and capsaicin content of the dried chili. For the free radical scavenging activity, there was no significantly different on chili fumigation with ozone for 30 min. The SEM image showed that the rougher structure of chili surface was observed after ozone treatment, possibly due to the ozone corrosive effect. The conclusive diagram for the 1st part of is as shown in Figure 30.



Objective of Part I.

To study the pesticides degradation efficiency on dried chili under gaseous ozone fumigation and the effect of gaseous ozone fumigation to physical and chemical properties of dried chili.

01 **Pesticide degradation on dried chili**
Results showed that gaseous ozone degraded equivalent to 99.9% shorter half-life period as compared to non-ozone degradation.

02 **Effect of Capsaicin content and Physical property**
Ozone fumigation process didn't significantly affect ($p \geq 0.05$) to capsaicin, water activity and color of dried chili

03 **Effect of TPC and Free radical scavenging activity**
Ozone fumigation process slight affect to TPC but didn't effect to antioxidant which analyzed by DPPH method.

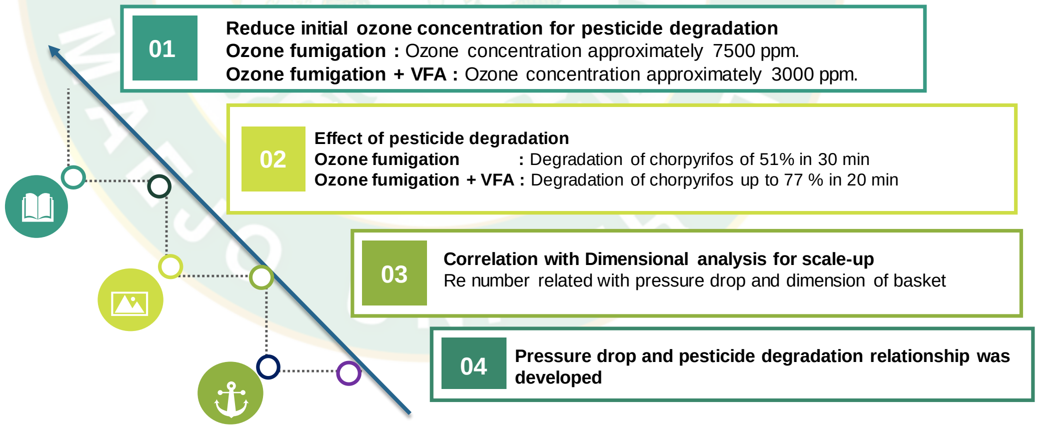
04 **Effect of Surface morphology**
Ozone fumigation process increased the roughness structure of chili surface.

Figure 30 Conclusive diagram of the research finding from Part 1

In the second part, the gaseous ozone fumigation using a novel VFA circulation technique was developed to reduce the chlorpyrifos pesticide residue on dried chili. The VFA circulation was studied in terms of dimensionless parameters and Buckingham PI – theorem. It was found that the Reynolds number (Re) exhibited a relationship with Hydraulic diameter (D_H) the dried chili basket. The OVFA fumigation can reduce pesticide residue up to 77% within 20 min, whereas the ozone fumigation without VFA circulation exhibited only 45% pesticide residue degradation. The VFA is accounted for the efficiency improvement by 26% on pesticide degradation and save operation cost by 34% compared to the non-VFA fumigation. Lastly, to simplify a further application of pesticides degradation using ozone fumigation and vertical forced-air circulation model, the relationship of pressure drop and pesticide degradation efficiency was determined. Therefore, the development of gaseous ozone fumigation using a novel VFA circulation technique to reduce chlorpyrifos pesticide residue in dried chili was summarized in the conclusive diagram as shown in Figure31.

Objective of Part II.

To develop gaseous ozone fumigation on dried chili using a novel vertical forced-air (VFA) circulation technique.



01 **Reduce initial ozone concentration for pesticide degradation**
Ozone fumigation : Ozone concentration approximately 7500 ppm.
Ozone fumigation + VFA : Ozone concentration approximately 3000 ppm.

02 **Effect of pesticide degradation**
Ozone fumigation : Degradation of chorpyrifos of 51% in 30 min
Ozone fumigation + VFA : Degradation of chorpyrifos up to 77 % in 20 min

03 **Correlation with Dimensional analysis for scale-up**
Re number related with pressure drop and dimension of basket

04 **Pressure drop and pesticide degradation relationship was developed**

Figure 31 The conclusive diagram of research finding from Part 2.

Lastly, the experimental results in this research proved that gaseous ozone fumigation can be an alternative to effectively reduce pesticide residue in chili and other agricultural products in order to improve food qualities and safety. It can be finally concluded that the OVFA exhibits a great potential to be further developed as a rapid method to decay the pesticide residue in dried chili in the industrial scale. This system could be further applied in other dried agricultural products or herbs as well.

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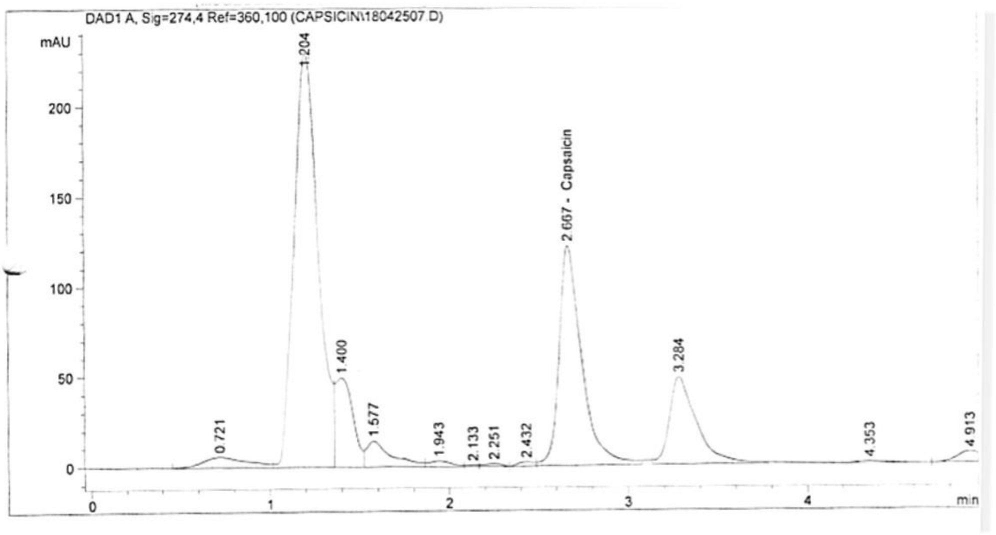
APPENDIX

APPENDIX A

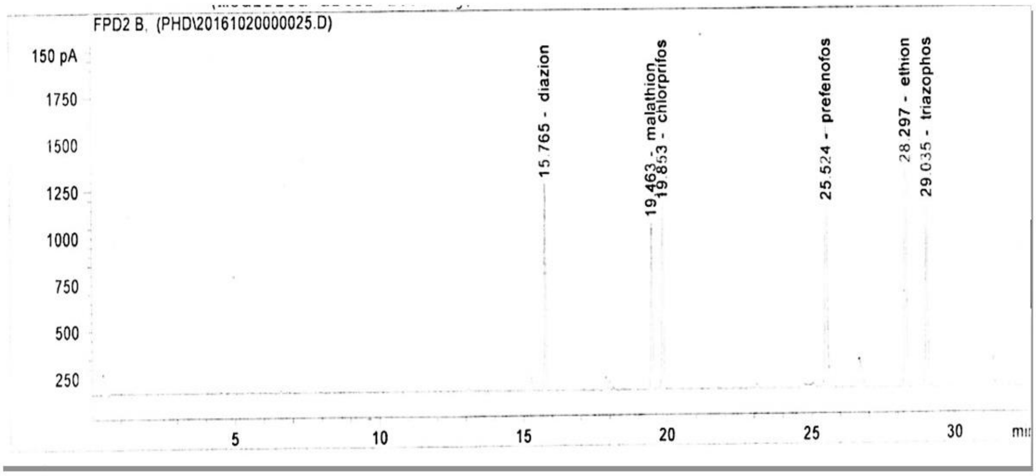
Analytical of capsiacin and pesticide residue

High performance liquid chromatography (HPLC)



Chromatogram of Capsaicin

Gas chromatography (GC)



Chromatogram of Diazion, Malathion, Chlorpyrifos, Profenofos, Ethion and Triazophos

APPENDIX B

Research publication

OZONE: SCIENCE & ENGINEERING
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Effect of gaseous ozone fumigation on organophosphate pesticide degradation of dried chilies

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ABSTRACT
The objective of this work was to study the effects of ozone fumigation on pesticides' residue degradation in dried chilies while maintaining its qualities. Gaseous ozone with a gas rate of 5.5 g/h was applied to four organophosphate pesticides for 5 to 30 min. The degradation kinetics of the pesticide residue was then analyzed. The results showed that gaseous ozone degraded malathion, chlorpyrifos, profenofos, and ethion with half-life periods ($t_{1/2}$) of 17.4, 27.4, 34.1, and 18.0 min, equivalent to 99.9% shorter half-life period as compared to non-ozone degradation. Furthermore, ozone fumigation did not significantly affect ($p \geq 0.05$) the water activity, color, and capsaicin content of dried chilies.

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Degradation Kinetics; Dried Chili; Half-Life Period; Ozone; Pesticide Residue

1. Introduction

Thailand is one of the world's leading exporters of agricultural products (Panuwet et al. 2012) and the global demand for these products is increasing due to world population growth. For example, world rice consumption in 2017 was predicted to be 480.1 million tons, an increase of 1.4 million tons from 2016 (Popp, Pető, and Nagy 2013; United States Department of Agriculture 2017). Due to the limitations in the expansion of agricultural farmland, farmers need to increase their crop yield on the existing farmland to achieve future demands (Popp, Pető, and Nagy 2013).

Pests are a major cause of crop yield losses. In order to control plant pest in agriculture and to minimize crop yield losses, pesticides have been extensively used in greater amounts over time (Blankson et al. 2016; Oerke and Dehne 2004; Ooraikul et al. 2011; Panuwet et al. 2012). Consequently, pesticide residues have been detected in most Thai agricultural products, including chilies, as a result of high pesticide application rates (Harnpicharnchai, Chaiear, and Charerntanyarak 2013). Organophosphates are highly effective and inexpensive and they are one of the most widely used, general purpose pesticides in Thailand (Harnpicharnchai, Chaiear, and Charerntanyarak 2013; Ooraikul et al. 2011). Nevertheless, organophosphates are highly toxicity, and they leave residue that is harmful to humans, causing health problems, such as respiratory and myocardial problems, and neuromuscular transmission impairment (Chowdhury et al. 2012; Clarke et al. 1997; Damalas and Eleftherohorinos 2011; Duangchinda, Anurugsa, and Hungspreug 2014; Issa et al. 2010; Oerke and Dehne 2004; Ooraikul et al. 2011; Wilson and Tisdell 2001).

Chili is an important agricultural product of Thailand and it is used as a basic ingredient in daily cooking all over the world. Thailand produces large quantities of chili and exports it as a fresh or dried product. The amount of chili exported has been increasing annually (Kaewkiew, Nabnean, and Janjai 2012; Nathakaranakule et al. 2006) and organophosphate pesticide residues have been found in much of the chili crop (Ooraikul et al. 2011). Özbey, Karagöz, and Ali (2017) reported that the half-lives of the major organophosphate derivatives (chlorpyrifos, diazinon, and methidathion) are 5.64, 6.42, and 5.25 days in grapes, while their half-life in natural sun dried chilies was reported to be 5 days (Kaewkiew, Nabnean, and Janjai 2012). Even though pesticide residues can be degraded naturally by sunlight, this requires at least 5 days of the sun drying process. Thus, the development of a more efficient method of pesticide residue degradation in chilies is desirable in order to meet the necessary safety and quality standard of exporting agricultural products.

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Several techniques have been reported on the reduction of pesticide residues in agricultural products; these include: ozone fumigation (Botondi et al. 2015; Gabler et al. 2010; Heleno et al. 2014; Msayleb and Ibrahim 2011; Tabakoglu and Karaca 2015), UV photolysis (Chelme-Ayala, El-Din, and Smith 2010; Garbin et al. 2007; Kowalska et al. 2004; Zhang, Wilson, and Danielson 2008), semiconductor photocatalysis (Hashimoto et al. 2016; Hurum et al. 2003; Lannoy et al. 2017), electrochemical oxidation (Guelfi et al. 2017, Rubí-Juárez et al. 2016), and Fenton oxidation (Saini et al. 2016; Sedaghat et al. 2016). However, none of these approaches have been reported as being used on dried chilies.

Ozone fumigation is one of the most prominent techniques used for reducing the pesticide residue that produces no secondary pollutant (Botondi et al. 2015; Chen, Lin, and Kuo 2013; Jasim et al. 2006). Ozone is a strong oxidizing agent that is inexpensive, commercially available, and environmentally friendly (Kırış, Velioglu, and Tekin 2017). The product of ozone degradation is oxygen, thus, it does not leave behind toxic residues on the treated products (Botondi et al. 2015). The use of ozone in the degradation of pesticides can be achieved by using either gaseous ozone or ozonated water (Ikehata and Gamal El-Din 2005; Smilanick, Margosan, and Mlikota Gabler 2002; Whangchai et al. 2011). Whangchai et al. (2011), however, reported that gaseous ozone was more effective than ozonated water in the degradation of chlorpyrifos (Whangchai et al. 2011). Moreover, gaseous ozone is a more appropriate alternative for the application on dried agricultural products.

In this work, gaseous ozone fumigation was proposed to degrade organophosphate pesticides on dried chilies. The objective of this work was to reduce organophosphate pesticides in dried chili samples using a gaseous ozone fumigation technique and to determine whether ozone fumigation affects chili qualities. The degradation kinetics of four organophosphate pesticides, namely malathion, chlorpyrifos, profenofos, and ethion in dried chili samples were analyzed. The half-life period of pesticide degradation, water activity, color, and capsaicin content of dried chili after being fumigated with ozone were also investigated.

2. Materials and methods

2.1. Preparation of pesticide coated-chili

Red dried chilies used in this study were obtained from a local farmer in Chiang Mai, Thailand. They were cultivated without chemical pesticides. To ensure that the samples were free of pesticide residues, the dried chilies were analyzed using a gas chromatograph (model 6890N, Agilent Technologies Canada Inc., Canada) equipped with a flame photometric detector (GC/FPD).

As for the pesticide application on the dried chilies, each treatment was accomplished in batches of 10 kg of dried chilies. The dried chilies were sprayed with 20 mL of organophosphate pesticides mixture solution. The mixture solution contained 1000 mg/L of each pesticide, namely malathion, chlorpyrifos, profenofos, and ethion (Dr. Ehrenstorfer GmbH., Germany). Then, the samples were dried at ambient temperature (25°C/60% RH) for 10 h before ozone treatment.

2.2. Ozone treatment

Five hundred grams of red dried chili samples were packed in a 25 L polycarbonate container for ozone fumigation as shown in Figure 1. The gaseous ozone was generated at an ozone rate of 5.5 g/h via an ozone generator using a corona discharger with O_2 input flow rates of 7.5 L/min and back pressures of 12 kPa (Changchai, Varith, and Jaturonglumlert 2015). The pesticide coated chili samples were fumigated with ozone gas for 0, 5, 10, 15, 20, 25, and 30 min. The pesticide-coated chilies without ozone treatment were separated as a control. After ozone treatment, all chili samples were packed in low-density polyethylene bags and stored at 25°C for 8 weeks for studying the qualities and pesticide half-life kinetics.

2.3. Analysis of the organophosphate pesticide residue

The extraction of chili samples for the determination of the organophosphate pesticide residue was performed with organic solvents and salts ($MgSO_4$ and NaCl), and clean-up sorbents were used for dispersive solid phase extraction according to the QuEChERS method

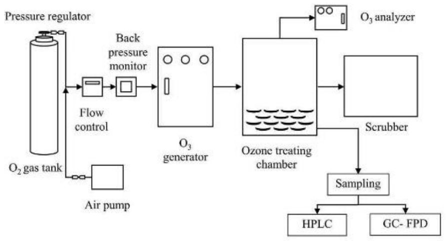

Figure 1. Schematic diagram of gaseous ozone fumigation equipment.

(Grimalt and Dehouck 2016). About 40 mL of AR graded acetonitrile (RCI labscan, Thailand) was added into 10 g of each dried chili sample. Then, they were homogenized at 20,000 rpm for 2 min. The volume of samples was adjusted to 50 mL with acetonitrile. The samples were shaken together with 5 grams of anhydrous magnesium sulfate and 1.5 g of sodium chloride for 1 min. The supernatant was transferred to a 50 mL centrifuge tube, containing 0.2 g of primary secondary amine (PSA), 3.0 g of anhydrous magnesium sulfate, and 0.2 g of activated charcoal for cleanup. The extract was centrifuged at 2,500 rpm for 10 min and 10 mL of supernatant (purified extract) was transferred to a test tube and later evaporated using a nitrogen evaporator. The volume of the sample was adjusted to 5 mL using ethyl acetate and then filtered through a 0.45-μm nylon membrane filter into a 2 mL vial. A gas chromatograph (model 6890N, Agilent Technologies Canada Inc., Canada) equipped with a flame photometric detector (GC-FPD) was used for pesticide residue determination. The pesticide residue was analyzed by GC-FPD using an HP-5 capillary column with particle sizes of 0.25 μm and 30 m × 0.32 mm diameter. Helium gas was used as a carrier gas with a flow rate of 1.5 mL.min^{-1}. Initially, the oven temperature was 80°C for 2 min, then it was ramped to 150°C at 25°C.min^{-1} and held for 5 min, ramped to 190°C at 5°C.min^{-1} and held for 5 min, ramped to 220°C at 10°C.min^{-1} and held for 5 min, and finally ramped to 250°C at 10°C.min^{-1}, respectively.

2.4. Physical properties of the measurement

The water activity (a_w) is relevant to the quality of dried food due to its importance in the stability of food. For most foods, the critical point of water activity at which microorganisms cannot grow is in the range of 0.6–0.7 (Bonazzi and Dumoulin 2011). The water activity was measured using an AquaLab water activity meter (model 3TE, Decagon devices, USA). About 0.5 g of fumigated dried chili samples were cut into small pieces of approximately 5 × 5 mm. They were then put into a plastic holder of the water activity meter. The determination of the water activity was carried out at ambient temperature (Calvache et al. 2015).

Color is part of the visual appearance that involved the quality of dried food (Bonazzi and Dumoulin 2011). The CIE L*a*b* color scale was used as color indices. L* represents the luminance or lightness component, ranging from 0 to 100 (from black to white). The a* and b* values are the two chromatic components, ranging from −120 to 120 (from green to red) and from −120 to 120 (from blue to yellow), respectively (Acevedo et al. 2008; Pedreschi et al. 2007). The total color difference, ΔE, was also used to determine a change in color after fumigation. ΔE was calculated using Equation 1, where L_0, a_0, and b_0 were standard color values (Torres et al. 2011).

$$\Delta E = \sqrt{(L^* - L_0)^2 + (a^* - a_0)^2 + (b^* - b_0)^2} \qquad (1)$$

For color measurements, the samples were cut lengthwise and spread out to be measured for color indices using a spectrophotometer (model MiniScan XE PLUS 45/0-S, Hunter Lab, USA). The color scale was presented using the CIE system in terms of L* (lightness), a*(redness and greenness), and b*(yellowness and blueness).

2.5. Analysis of capsaicin

All chili samples were extracted and the determination of capsaicin was done using the HPLC technique (Collins, Wasmund, and Bosland 1995). For capsaicin extraction, 40 mL of acetonitrile (RCI labscan, Thailand) was added into 10 g of each dried chili. Then, they were homogenized at 20,000 rpm for 2 min. The volume of the samples was adjusted to 50 mL with acetonitrile. All samples were stored at 4–8°C for 24 h. Finally, the supernatant layer of each sample was filtered through 0.45 μm nylon filter paper into a vial using a 2 mL disposable syringe (Millipore, Bedford, MA, USA). Capsaicin analysis was carried out by HPLC (model 1100 Series, Agilent Technologies Canada Inc., Canada) using a UV-diode array detector (UV-DAD) at 274 nm. Separation was achieved using a ZORBAX Eclipse XDB C-18 reverse-phase column (5 μm) with a particle size of 150 mm and 4.6 mm internal diameter (Agilent Technologies Canada Inc., Canada) and 10 μL was automatically injected into the system and was eluted using an isocratic mobile phase (acetonitrile/DI water 70:30 (v/v)) at a 1mL/min flow rate.

2.6. Determination of pesticide degradation kinetics

The rate constant of degradation and half-life period of each organophosphate pesticide were analyzed using Equations 2 and 3, respectively.

$$\ln\frac{[C]}{[C_0]} = -kt \qquad (2)$$

C represents the concentration of the pesticide (mg/kg), t represents the treatment time (min), k represents the rate constant of degradation of the pesticide, and subscript 0 represents the initial time zero. In order to determine the half-life period ($t = t_{1/2}$) of each organophosphate pesticide, the concentration of a pesticide at half-life period is determined by $[C] = [C_0]/2$.

Therefore, Equation 2 is further derived as shown in Equation 3 (Alighourchi and Barzegar 2009).

$$t_{1/2} = \frac{0.693}{k} \qquad (3)$$

2.7. Statistical analysis

Samples from each treatment were statistically analyzed using the Statistics Package for the Social Sciences (SPSS, IBM Corp., USA) by one-way analysis of variance (ANOVA). Duncan's method was used to analyze the significant difference of responses at $p < 0.05$.

3. Results and discussion

3.1. Analysis of the organophosphate pesticide residue

The degradation of four organophosphate pesticides, namely malathion, chlorpyrifos, profenofos, and ethion, was studied. During the storage of the chili products, self-degradation of pesticides took place without any ozone fumigation. Therefore, the degradation of organophosphate pesticides under ozone fumigation was compared to self-degradation as shown in Figure 2.

The degradation of organophosphate pesticides, self-degradation, and degradation with ozone fumigation are shown in Figure 2(a,b). It is found that ozone accelerated the degradation of organophosphate pesticides in all the chili samples. After 8 weeks of storage, malathion, chlorpyrifos, profenofos, and ethion were degraded by 46, 39, 42, and 28%, respectively. On the other hand, with the ozone fumigation for 30 min, malathion, chlorpyrifos, profenofos, and ethion were degraded by 68, 51, 45, and 66%, respectively. Since ozone is a promising oxidant due to its high oxidation potential value of 2.07 V (Ikehata and El-Din 2006), it allows for a great degradation rate on pesticides that are synthetic chemical substances. Therefore, the degradation of pesticides under ozone fumigation is found to be much faster than the degradation without ozone fumigation. The comparison between the self-degradation of pesticides and degradation by ozone fumigation is shown in Figure 3.

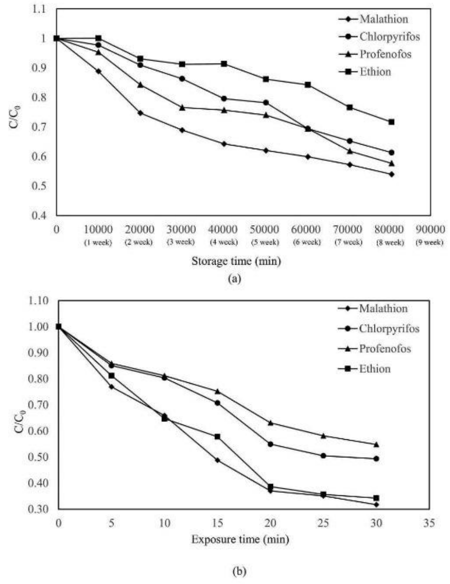

Figure 2. Organophosphate pesticide degradation: (a) self-degradation during storage at 25°C without ozone fumigation and (b) accelerated degradation with ozone exposure.

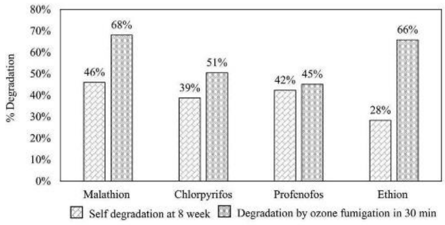

Figure 3. Comparison between self-degradation and degradation of organophosphate pesticides by ozone fumigation.

Self-degradation kinetics of four organophosphate pesticides is considered to be the first-order reaction, as shown in Figure 4(a,b). The obtained parameters are presented in Table 1. The degradation rate constants (k) of malathion, chlorpyrifos, profenofos, and ethion on non-ozone fumigated chilies are 7.22×10^{-6}, 6.35×10^{-6}, 6.54×10^{-6}, and 3.98×10^{-6} mg/kg/min, respectively. Meanwhile, the degradation rate constants (k) of malathion, chlorpyrifos, profenofos, and ethion on ozone fumigated chilies are 3.99×10^{-2}, 2.53×10^{-2}, 2.03×10^{-2}, and 3.84×10^{-2} mg/kg/min, which are approximately 10,000-fold different in the order of magnitude. Both non-ozone and ozone fumigated chilies exhibit similar trends of pesticide residue degradation. The higher degradation rate constant reflected the shorter time for the pesticide residue to decay. The results correspond well with the previous work by Bourgin, Marc, 2013 (Bourgin, Albet, and Violleau 2013) who reported that the degradation of pesticides on moistened wheat seeds by ozonation fumigation for

Table 2. Water activity and color of the dried chilies after ozone fumigation.

Exposure time (min)	Water activity$^{(n.s)}$, a_w	Color qualities$^{(n.s)}$			
		L*	a*	b*	ΔE
0	0.66 ± 0.02	35.22 ± 4.40	26.63 ± 5.01	13.61 ± 5.07	-
5	0.63 ± 0.01	29.60 ± 0.92	29.89 ± 1.30	16.24 ± 0.31	7.05 ± 1.33
10	0.69 ± 0.00	32.20 ± 3.84	25.91 ± 2.74	12.77 ± 1.77	3.95 ± 4.18
15	0.67 ± 0.01	32.01 ± 1.52	24.33 ± 4.07	11.90 ± 3.91	6.21 ± 2.05
20	0.66 ± 0.01	29.17 ± 5.13	26.69 ± 5.94	14.46 ± 2.58	8.58 ± 3.73
25	0.62 ± 0.05	29.13 ± 1.98	26.07 ± 4.41	12.31 ± 3.32	7.83 ± 0.60
30	0.65 ± 0.02	30.93 ± 3.49	24.43 ± 4.14	11.25 ± 2.42	8.05 ± 1.39

n.s. = not significantly different ($p \geq 0.05$).
Exposure time at 0 min refers to non-ozone fumigation.

during disinfestation of fruit fly larvae in fresh chilies using ozone fumigation. Normally, ozone has a color bleaching effect (increasing lightness, L*) (Aday and Caner 2014) on fresh products that contain a high amount of free water content. The high water content products are more susceptible to the bleaching of color than dried products. In this study, the dried chilies contain a low amount of free water content as indicated by the low water activity. It limits the chemical reaction that would cause the bleaching effect. Therefore, lightness of the dried chilies in this work remained unchanged.

3.3. *Analysis of capsaicin*

Table 3 indicates that the capsaicin content of the dried chilies tended to decrease with increasing exposure time, but not statistically different ($p \geq 0.05$). After ozone fumigation, the dried chilies which contain an initial capsaicin content of 3,205 mg/kg decreases to 3,095, 3,080, 3,035, 3,030, 2,833, and 2,832 mg/kg upon a 5-min increment of fumigation time. From a previous report, capsaicin is found mainly in the ovary part of chilies (Supalkova et al. 2007). Thus, it is possible that the ozone fumigation given is not long enough to allow ozone gas to penetrate into the chili ovary, which results in a non-significant difference in the capsaicin content due to the ozone exposure time of within 30 min. As ozone is a strong oxidizing agent, it may affect the quality of food such as color loss and degradation of a phenolic compound and antioxidant compound (Karaca and Sedat Velioglu 2014). Therefore, the exposure time of ozone fumigation is an important key that should be considered in order to avoid quality change. The results show that a gaseous ozone fumigation time of 30 min can be used to degrade organophosphate pesticides without any significant change in chili qualities, which corresponds to the result of previous reports, which show that ozone is used to reduce pesticides in lychee effectively without any weight loss and soluble solid change (Whangchai et al. 2011). Thus, it is suggested that for further development of the ozone fumigation process, the dried chilies should be exposed to ozone gas for no longer than 30 min to maintain their quality and capsaicin content.

Table 3. Capsaicin content of the dried chilies after ozone fumigation.

Exposure time (min)	Capsaicin content$^{(n.s)}$ (mg/kg)
0	3,205 ± 317
5	3,095 ± 182
10	3,080 ± 293
15	3,035 ± 148
20	3,030 ± 154
25	2,833 ± 476
30	2,832 ± 218

n.s. = not significantly different ($p \geq 0.05$).

4. Conclusion

Gaseous ozone fumigation is successfully used to degrade four organophosphate pesticides, namely malathion, chlorpyrifos, profenofos, and ethion in dried chilies. The degradation kinetics of the organophosphate pesticides is found to be a first-order reaction. Gaseous ozone is able to degrade malathion, chlorpyrifos, profenofos, and ethion with $t_{1/2}$ values of 17.4, 27.4, 34.1, and 18.0 min, respectively. Without ozone fumigation, the $t_{1/2}$ values are 66.6, 75.7, 73.5, and 120.9 days, which are more than 99% difference compared to the ozonated chilies. Ozone fumigation did not significantly affect ($p \geq 0.05$) the water activity, color, and capsaicin content of the dried chilies. Ozone fumigation exhibits great potential to be further developed as a rapid method to decay the pesticide residue in dried chilies.

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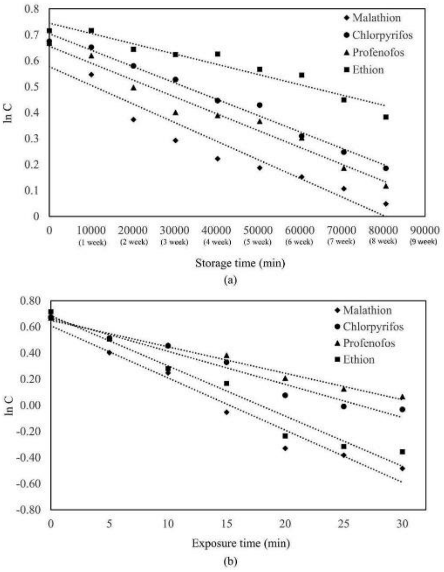

Figure 4. First-order kinetics plot of the organophosphate pesticide degradation: (a) self-degradation during storage at 25°C without ozone fumigation and (b) accelerated degradation with ozone exposure.

96 min was the first-order reaction with a degradation percentage of 99% on imidacloprid and 90% on bitertanol.

In terms of the degradation half-life period ($t_{1/2}$), chilies without ozone fumigation exhibit $t_{1/2}$ for malathion, chlorpyrifos, profenofos, and ethion of 66.6, 75.7, 73.5, and 120.9 days, respectively. On the other hand, chilies with ozone fumigation exhibit the $t_{1/2}$ value for the degradation of malathion, chlorpyrifos, profenofos, and ethion of 17.4, 27.4, 34.1, and 18.0 min. The results clearly show that the ozone gas dramatically degraded four organophosphate pesticides with a difference in the $t_{1/2}$ value up to 99.9% in dried chilies.

It is noted that the k value, which is a slope of the first-order kinetic equation according to Equation 2, exhibits a proportional relationship with the reaction rate. As the k value increases, the degradation rate of pesticide increases. On the other hand, the k value exhibits an inverse relationship to the $t_{1/2}$ value. With a shorter half-life period, the pesticide residue degrades in a shorter time. Hence, the effective process to degrade the pesticide residue in dried chilies should possess a high value of k and a small value of $t_{1/2}$, which was achieved by ozone gas fumigation in this work.

3.2. Measurement of physical properties

The water activity of dried chilies after ozone fumigation is found to be in the range of 0.62–0.69 as shown in Table 2. The ozone fumigation did not significantly affect ($p \geq 0.05$) the water activity of the dried chilies compared to the non-fumigated dried chilies. Since the water activity is an indicator of free water, the low water activity also indicates the low free water existing inside the dried chilies. Due to the low free water content in the dried chilies, it is possible that the oxidation reaction that occurred during ozone fumigation was not dominated by a chemical reaction between ozone and free water. However, the oxidation reaction taking place during ozone fumigation of dried chilies was likely to be dominated by a chemical reaction between the ozone and pesticides, which were coated on the outer skin of the chilies. As a result, the water activity of the dried chilies did not significantly change ($p \geq 0.05$) after ozone fumigation.

The color of the dried chilies after ozone fumigation for 0, 5, 10, 15, 20, 25, and 30 min is indicated by lightness (L*), redness (a*), and yellowness (b*). It is found that L*, a*, and b* values were not significantly different ($p \geq 0.05$), meaning that ozone fumigation did not significantly affect ($p \geq 0.05$) the color of the dried chilies. This was confirmed by the non-significant difference ($p \geq 0.05$) of the total color difference ΔE as well. The results of this study correspond to the previous work reported by Changchai, Varith, and Jaturonglumlert (2015) who report that the color of a fresh chili fruit was not affected by ozone treatment

Table 1. Kinetics parameters for the degradation of the organophosphate pesticides during storage at 25°C (without ozone fumigation) and with ozone fumigation.

	Non-ozone fumigation			Ozone fumigation			
Pesticide	k (mg/kg/min)	R^2	$t_{1/2}$ (day)	k (mg/kg/min)	R^2	$t_{1/2}$ (min)	Half-life time difference (%)
Malathion	7.22×10^{-6}	0.92	66.6	3.99×10^{-2}	0.95	17.4	99.9%
Chlorpyrifos	6.35×10^{-6}	0.98	75.7	2.53×10^{-2}	0.94	27.4	99.9%
Profenofos	6.54×10^{-6}	0.96	73.5	2.03×10^{-2}	0.98	34.1	99.9%
Ethion	3.98×10^{-6}	0.93	120.9	3.84×10^{-2}	0.96	18.0	99.9%

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APPENDIX C

Research publication

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Degradation Kinetics of Diazinon and Triazophos Pesticides in Dried Chili under Gaseous Ozone Fumigation

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ABSTRACT

Dried chili is normally contaminated with pesticide residue as a result from the excessive uses of pesticide in the field. The objective of this study was to determine the degradation kinetics of diazinon and triazophos pesticides in dried chili due to the oxidative potential of gaseous ozone fumigation. Both pesticides were spray-coated on dried chili and later fumigated with gaseous ozone at concentration rate of 5.5 g/hr for 30 min. Results showed that the degradation kinetic of diazinon and triazophos pesticides were presented on the first-order kinetic reaction. After 30 min of ozone fumigation, diazinon and triazophos residues were decreased by 69% and 47% with the half-life ($t_{1/2}$) of 17.9 and 32.1 min, respectively. Scanning electron microscopy (SEM) images indicated that ozonated chili exhibited more rough surface morphology than unozoned chili. Ozone fumigation can be further developed as pesticide scrubber on agri-foods due to it high efficiency in term of shortening of half-life period and rapid pesticide decay rate.

Keywords: Degradation kinetics, diazinon, dried chili, half-life period, ozone, triazophos

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INTRODUCTION

Dried chili is a popular spice product that is commonly used as ingredient for food flavoring and coloring (Jitbunjerdkul & Kijroongrojana, 2007; Toontom et al., 2012). Conventionally, dried chili is obtained by natural sun drying which takes about 7-20 days until moisture content decreased to 10-15% (Condorí et al., 2001; Öztekin et al., 1999; Toontom et al., 2012). The persistence problem remains as dried chili product in current market contains high level of pesticide residues (Pérez-Olvera et al., 2011). The pesticide contamination in chili product is due to the use of pesticide to increase crop production during agriculture of farmers (Ormad et al., 2010; Popp et al., 2013). Even if the drying process can help to degrade pesticide residue, it takes a long period (Özbey et al., 2017). A previous work reported that 59.3% of vegetables from farms and 13.2% of vegetables from markets contained organophosphorus pesticide residues at or above the maximum residue limits of the European Union (Sapbamrer & Hongsibsong, 2014). Despite the fact that organophosphates pesticides residue can be naturally degraded, Rasmusssen et al. (2003) mentioned that organophosphates chlorpyrifos, diazinon and fenitrothion could be reduced only 25 69% during storage for 79 days. In order to create a safe dried chili product, pesticide residues degradation prior to export is a proper approach.

Gaseous ozone utilization is one of the most prominent technique to reduce pesticide efficiently. It is able to be applied by either ozonated water or gaseous ozone (Mezzanotte et al., 2005; Smilanick et al., 2002; Whangchai et al., 2011). However, a study indicated that gaseous ozone exhibited higher degradation activity than ozonated water (Whangchai et al., 2011). This study aimed to study the degradation kinetic of diazinon and triazophos pesticide residues using gaseous ozone fumigation treatment. The effect of ozone treatment to chili surface, total phenolic compounds and antioxidant properties were also conducted to ensure the product qualities after ozone treatment.

MATERIALS AND METHODS

Dried Chili Sample Preparation

Pesticide-free red dried chili samples used in this study were purchased from USDA Certified farm. Ten kg of dried chili samples were coated with 20 mL of pesticide solution containing 1,000 mg/L of diazinon and 1,000 mg/L of triazophos (Dr.ehrenstorfer GmbH., Germany). The pesticide coated chillies were then allowed to dry at room temperature for 10 h.

Ozone Fumigation Treatment

Red dried chili samples were treated with ozone by loading of 500 g of red dried chili samples into a fumigation chamber (Figure 1). The chamber was filled with gaseous ozone with a flow rate of 5.5 g/hr. Corona discharger with O_2 flow rate of 7.5 L/min and back pressure of 12 kPa was used to generate ozone (Changchai et al., 2015). The pesticide coated dried chilies were treated with gaseous ozone for 0, 5, 10,15, 20, 25 and 30 min. Pesticide coated chili without ozone treatment was used as a control. After the fumigation process, dried chili samples were kept in low density polyethylene (LDPE) bags at 25ºC prior to evaluating the chemical, physical properties and kinetics degradation of pesticides.

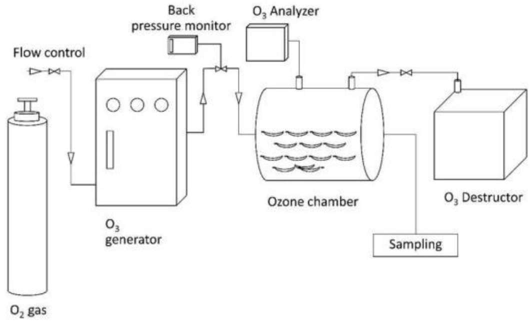

Figure 1. Gaseous ozone fumigation experimental setup

Diazinon and Triazophos Pesticide Residue Determination

The extraction of dried chili samples for the determination of diazinon and triazophos pesticide residue was achieved by QuEChERS technique using dispersive solid phase extraction (Grimalt & Dehouck, 2016). Pesticide residue determination was carried out using gas chromatograph equipped with flame photometric detector (GC/FPD, 6890N, Agilent Technologies Canada Inc.) using HP-5 capillary column (0.25 µm particle size, 30 m x 0.32 mm i.d., Agilent Technologies Canada Inc.,). Helium gas with a flow rate of 1.5 mL.min^{-1} was used as a carrier gas. The oven temperature was set up at 80°C for 2 min, then it was increased to 150°C at the rate of 25°C.min^{-1} and was held for 5 min. After that it was increased to 190°C at the rate of 5°C.min^{-1}, held for 5 min, ramped up to 220°C at the rate of 10°C min^{-1}, held for 5 min, and finally ramped up to 250°C at the rate of 10°C.min^{-1}, respectively.

Evaluation of Diazinon and Triazophos Pesticides Degradation Kinetic

The rate constant of diazinon and triazophos degradation and half-life period of pesticide degradation were evaluated using Equations 1 and 2, respectively.

$$\mathbf{h}\,\frac{[C]}{[C_0]} = -k \qquad [1]$$

C_0 is initial concentration of pesticide at treatment time = 0 (mg/kg), C is concentration of pesticide at treatment time = t (mg/kg), k is rate constant of the pesticide degradation, t is treatment time (min). In order to obtain the half-life period ($t=t_{1/2}$) of each pesticide, a pesticide with concentration at half-life period is determined by $[C] = [C_0]/2$. Therefore, half-life period could be calculated as shown in Equation 2 (Alighourchi & Barzegar, 2009).

$$t_{1/2} = \frac{0.693}{k} \qquad [2]$$

Determination of Total Phenolic Content (TPC)

The content of total phenolic compound (TPC) was studied using the Folin-Ciocalteu assay (Kovacova & MaliNoVá, 2007), with slight modification. Firstly, methanolic extract solution was prepared by mixing 5 g of sample with 20 ml of 70% methanol. The mixture was kept overnight at -20°C. Then the sample was adjusted final volume to 50 ml and was centrifuged at 2,500 rpm, 4°C for 10 min. The mixture of 0.5 ml of 50% Folin-Ciocalteu, 1 ml of 95% ethanol, 1 ml of methanolic extract, and 5 ml of reverse osmosis water was mixed and was kept at room temperature (25± 5°C) for 5 min. After that, 1ml of 5% (w/v) of sodium carbonate solution was added. The mixture was homogenized and was kept at room temperature for 60 min. TPC was analyzed using a NICOLET evolution 300 (Thermo Electron Eorporation, USA) spectrophotometer at 725 nm. The standard calibration curve was plotted using gallic acid at the concentration of 10 200 mg/L. The TPC was presented as gallic acid equivalent (GAE) mg/100g.

Determination of Free Radical Scavenging Activity

The determination of scavenging activity of dried chili extract was carried out based on 2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical scavenging assay (Milardović et al., 2006). The 2 ml of chili extract was mixed with 1 mL of 100 µM DPPH solution which was dissolved in 80% methanol. The mixture was then shaken vigorously and was kept in a dark room for 30 min at room temperature. The absorbance was evaluated using a spectrophotometer (Thermo Electron Corporation, NICOLET evolution 300, USA). The detection was determined at 515 nm of wavelength using methanol as a blank solution. Triplicate analysis was done and their activity was expressed as Trolox equivalent (TEAE) in mg/100g.

Scanning Electron Microscopy (SEM) Analysis

SEM technique was used to examine microstructure of chili surface without and with ozone fumigation for 30 min. Dried chili peel (5x5 mm) sample was cut into a small piece. The sample was coated with gold with 20 nm thickness in an ion sputter coater model JFC-1200 (JEOL, Japan). The microstructure of chili surface was observed by SEM JSM-5410LV (JEOL, Japan) at 10 kV.

Statistical Analysis

In this experiment, the obtained data were statistically examined using the Statistics Package for the Social Sciences (SPSS, IBM Corp., USA) by one-way analysis of variance (ANOVA). Duncan's test is commonly used in agricultural research. It has a great power for statistical analysis. The significant difference of responses was determined at $p<0.05$ using Duncan's method.

RESULTS AND DISCUSSION

Diazinon and Triazophos Pesticide Residue Analysis

In this study, diazinon and triazophos pesticide residues of dried chili after ozone fumigation treatment were studied. They were compared with those of dried chili stored in a polyethylene bag without any fumigation. Figure 2 shows that after 30 min of ozone fumigation, diazinon and triazophos could be degraded 69 and 47%, respectively. For untreated dried chili sample, diazinon and triazophos could be degraded 40 and 42% after being stored in a polyethylene bag for 8 weeks. The reason behind this is that ozone is a strong oxidizing agent that can allow pesticide degradation (Ikehata & El-Din, 2006; Ikeura et al., 2011; Tiwari et al., 2010). Therefore, the degradation of pesticide with ozone fumigation exhibited higher efficiency than the degradation without ozone fumigation.

Determination of Diazinon and Triazopho Pesticides Degradation Kinetic

Kinetics parameters for degradation of diazinon and triazophos during storage at 25°C (without ozone fumigation) and with ozone fumigation were shown in Table 1. Degradation kinetics of diazinon and triazophos are considered to be the first-order reaction. The degradation rate constants (k) of diazinon and triazophos on ozone treated chili were 3.8×10^{-2} and 2.2×10^{-2} mg/kg/min, respectively. Meanwhile, the degradation rate constants (k) of diazinon and triazophos on untreated chili were 7.0×10^{-6} and 6.0×10^{-6} mg/kg/min, which were approximately 5,400 and 3,700 folds different in order of magnitude. The greater degradation rate constant revealed the shorter time for pesticide residue to decline. The results corresponded well with previous work by Bourgin et al. (2013) who reported that the degradation of pesticide by ozonation fumigation was the first-order reaction. For the degradation half-life period ($t_{1/2}$), untreated chili revealed the $t_{1/2}$ for diazinon and triazophos of 68.8 and 80.2 days, respectively. However, chilies with ozone fumigation exhibited $t_{1/2}$ value for the degradation of diazinon and triazophos of 17.9 and 32.1 min.

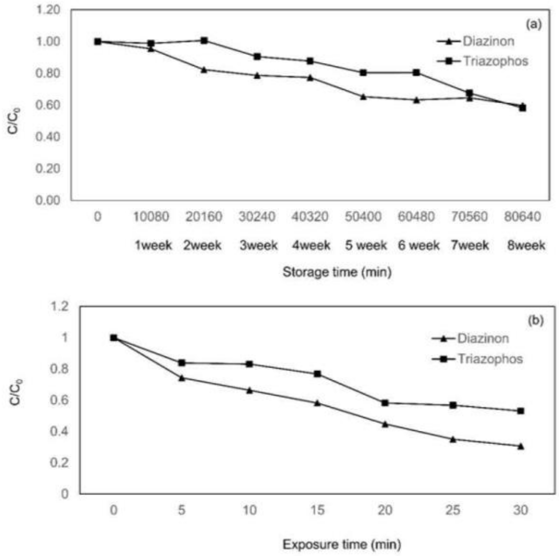

Figure 2. Diazinon and triazophos degradation by (a) self-degradation during storage at 25°C without ozone fumigation, and (b) accelerated degradation with ozone exposure.

Table 1

Kinetics study for degradation of the diazinon and triazophos during storage at 25°C (non-ozone fumigation) and with ozone fumigation

Pesticide	Non-ozone fumigation			Ozone fumigation			Half-life time difference (%)
	k (mg/kg/min)	R^2	$t_{1/2}$ (day)	k (mg/kg/min)	R^2	$t_{1/2}$ (min)	
Diazinon	7.0×10^{-6}	0.94	68.8	3.8×10^{-2}	0.99	17.9	99.9%
Triazophos	6.0×10^{-6}	0.88	80.2	2.2×10^{-2}	0.94	32.1	99.9%

Determination of Total Phenolic Content (TPC) and Free Radicals Scavenging Activity

The TPC and free radicals scavenging activity represent the quality of dried chili. The result of TPC in dried chili sample after fumigation for 30 min is shown in Table 2. The TPC tended to decrease due to fumigation time at 0, 5, 10, 15, 20 and 25 min but not significantly different ($p \geq 0.05$). However, after fumigation for 30 min, the TPC was significantly different ($p < 0.05$) from the others. This phenomenon occurred due to reaction of ozone and free radical (Misra et al., 2015; Sarangapani et al., 2017). For the free radical scavenging activity, there was not significantly different on fumigation 0 to 30 min as shown in Table 2. The results from this experiment corresponded to the previous reports (Alwi, 2017; Torres et al., 2011). It was found that total phenolic compound could be reduced by increasing of ozone concentration or time of fumigation.

Table 2

Total phenolic content and free radical scavenging activity in chili sample with ozone fumigation for 30 min.

Exposure time (min)	Total phenolic content (mgGAE/100g)	Free radical scavenging activity (mgTEAE/100g)$^{n.s.}$
0	150.27^{a} ± 8.62	51.01 ± 5.57
5	145.28^{a} ± 2.98	43.94 ± 0.61
10	147.81^{a} ± 6.86	51.69 ± 3.68
15	150.93^{a} ± 6.28	44.30 ± 0.81
20	150.83^{a} ± 5.01	51.73 ± 0.85
25	145.53^{a} ±9.77	44.33 ± 5.34
30	130.00^{b} ± 5.64	49.10 ± 1.22

*n.s. = not significantly different ($p \geq 0.05$).
*Values followed by the different letter within the same row are significantly different from each other ($p < 0.05$).

Scanning Electron Microscopy (SEM) Analysis

SEM image of chili surface without ozone fumigation was compared to chili surface with ozone fumigation for 30 min as shown in Figure 3. It was found that ozone affected surface of chili. The increasing of roughness structure of chili surface was observed after ozone treatment. This phenomenon cannot be clearly explained but it is possible that the ozone fumigation at high concentration may have oxidative reaction with some substance at surface causing the distort morphological changes as a rougher or corrosive surface of the chili (Alwi, 2017; O'Donnell et al., 2012).

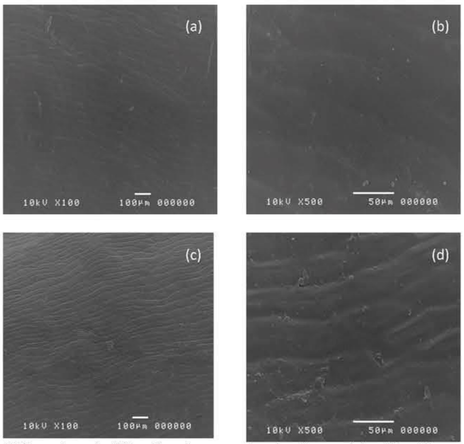

Figure 3. SEM image of chili surface (a, b) without ozone fumigation and (c, d) with ozone fumigation for 30 min.

CONCLUSIONS

Gaseous ozone treatment was succesfully used to degrade diazinon and triazophos in dried chili. The kinetic study revealed that first-order reaction of diazinon and triazophos degradation on ozone treated chili showed rate constants (k) of 3.8×10^{-2} and 2.2×10^{-2} mg/kg/min, respectively, which were approximately 5,400 and 3,700 folds different in order of magnitude compared to untreated chili. For the degradation half-life period ($t_{1/2}$), the untreated chili revealed the $t_{1/2}$ for diazinon and triazophos of 68.8 and 80.2 days, respectively. However, chili with ozone fumigation exhibited $t_{1/2}$ value for the degradation of diazinon and triazophos of 17.9 and 32.1 min. TPC was significantly different ($p<0.05$) after 30 min of ozone treatment. For the result of free radical scavenging activity, there was no significant difference on fumigation from 0 to 30 min. SEM image showed that roughness structure of chili surface was observed after ozone treatment, possibly due to the ozone corrosive effect. Since ozone fumigation shortens the $t_{1/2}$ diazinon and triazophos by 69 and 47%, it exhibits a promising protential to be applied for reducing the pesticide residues in dried chilli without significant changes in physical and chemical properties. Therefore, gaseous ozone fumigation can be an alternative to effectively reduce pesticide residue in chilli and other agricultural products in order to improve food qualities and safety.

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