THE EFFECT OF FRYING PROCESS AND SOME NATURAL ADSORBANTS ON ORGANOCHLORINE PESTICIDE RESIDUES FOR COMMON EDIBLE OILS IN EGYPTIAN MARKETS

By

Tamer Mahmoud Abd El-Aziz Mahmoud El-Mergawy
B.Sc. Agriculture (Pesticides Branch), Cairo University, 1999

A Thesis Submitted In Partial Fulfillment
Of
The Requirement For The Master Degree
In
Environmental Science

Department of Agricultural Science
Institute of Environmental Studies & Research
Ain Shams University

2012

APPROVAL SHEET

THE EFFECT OF FRYING PROCESS AND SOME NATURAL ADSORBANTS ON ORGANOCHLORINE PESTICIDE RESIDUES FOR COMMON EDIBLE OILS IN EGYPTIAN MARKETS

By

Tamer Mahmoud Abd El-Aziz Mahmoud El-Mergawy
B.Sc. Agric. Science (Pesticides Branch), Cairo University, 1999

This Thesis Towards a Master Degree In Environmental Science Has Been approved by:

Name	Signature
Prof. Dr. Ahmad Abd El Salam Barakat Professor of Chemistry and Toxicology of Pesticides, Faculty of Agriculture, Cairo University.	.....
Prof. Dr. Mohamed Farag Mohamed Nasr Khallaf Professor of Food Science and Technology, Faculty of Agriculture, Ain Shams University.	.....
Prof. Dr. Usama Mohamed Mohamed Radwan Professor of Food Science and Technology and Head of the Agricultural Science Department, Institute of Environmental Studies and Research, Ain Shams University.	.....

2012

THE EFFECT OF FRYING PROCESS AND SOME NATURAL ADSORBANTS ON ORGANOCHLORINE PESTICIDE RESIDUES FOR COMMON EDIBLE OILS IN EGYPTIAN MARKETS

By

Tamer Mahmoud Abd El-Aziz Mahmoud El-Mergawy
B.Sc. Agriculture (Pesticides Branch), Cairo University, 1999

A Thesis Submitted In Partial Fulfillment
Of
The Requirement for the Master Degree
In
Environmental Science

Department of Agricultural Science

Under the Supervision of:

Prof. Dr. Zidan Hendi Abd El-Hamid Zidan
Professor of Chemistry and Toxicology of Pesticides,
Faculty of Agriculture, Ain Shams University.

Prof. Dr. Usama Mohamed Mohamed Radwan
Professor of Food Science and Technology and Head of the Agricultural Science Department, Institute of Environmental Studies and Research, Ain Shams University.

Prof. Dr. Islam Noaman Nasr
Professor of Central Agricultural Pesticides Laboratory,
Agricultural Research Center.

2012

تأثير عمليات القلي وإستخدام بعض المدمصات الطبيعية على متبقيات المبيدات الكلورونية العضوية في الزيوت الغذائية الشائعة في الأسواق المصرية

رسالة مقدمة من

تامر محمود عبد العزيز محمود المرجاوي

بكالوريوس فى العلوم الزراعية (شعبة مبيدات) جامعة القاهرة ١٩٩٩

لاستكمال متطلبات الحصول على درجة الماجستير

فى العلوم البيئية

قسم العلوم الزراعية البيئية

معهد الدراسات والبحوث البيئية

جامعة عين شمس

٢٠١٢

ACKNOWLEDGMENTS

"I do THANKS to my God "**Allah**", the almighty, nothing I could put in writing would adequately describe my grateful thanks for giving me the strength and courage in going through this work successfully "

I would like to express my deeply gratitude to my supervisor, **Dr. Zidan Hendi Abd El-Hamid,** Professor of Chemistry and Toxicology of Pesticides, Faculty of agriculture, Ain Shams University, for his contribution to my scientific knowledge, continuous and generous support, guidance and friendship. Thanks **Dr. Zidan** you have had a far-reaching impact on my professional development. Many thanks for bringing me to this point in my academic career.

I would like to thank my supervisor,**Prof. Dr. Usama Mohamed Mohamed Radwan,** Head of the Agricultural Science Department, Institute of Environmental Studies and Research, Ain Shams University, and **Prof. Dr. Islam Noaman Nasr**, Professor in Pesticide Residues and Environmental Pollution Department and Head of the Central Analysis Unit, Central Agricultural Pesticides Laboratory, Agricultural Research Center, for their kind interest and help.

I would like to express my sincere appreciation to Prof. Dr. Fatma Ali Ahmed, Prof. of Photochemistry, Head of Phytochemistry Unit, Desert Research Center; and Dr. Ashraf Abo Hadid, for their belief in me; they gave me the keys to become a leading scientist someday.

I would like also to thank all of my wife, colleagues and friends in the Central Agricultural Pesticides laboratory, Agricultural Research Center, for their useful and friendly discussions.

I would like also to extend my thanks to Eng. Amr Gadallah, Senior Quality Assurance and Products Formulation Developments Manager, Savola Egypt Company, 10th of Ramadan City-Egypt.

ABSTRACT

The present investigation aimed to determine the characteristics of four edible oils before and after frying. Also, the collected samples of these oils from great Cairo governorate were analyzed by gas chromatography supplied by electron capture detector (GC-ECD) to determine the types and amounts of organochlorine pesticides. Moreover, the role of frying process on 180°C±5°C/7-12min and activated charcoal on the degradation / removal of the studied organochlorine pesticides were investigated.The obtained results indicated great differences in the standard specifications of the studied four oils before frying. Frying processes as shallow or deep-frying resulted in increasing acid, peroxide values of all oils, while decreased the values of iodine, saponification and esterification than the non fried oils. Frying processes variously decreased the induction period of the four studied edible oils when used with potatoes, falafel and eggplant. Analysis of oil samples by gas chromatography (GC) showed that the majority of the analyzed samples were found free from OCPs residues. The frequency of positive samples were 4.29, 5.00, 6.43 and 13.57 %, respectively. Frying processes and activated charcoal proved great role in reducing of OCPs residues from corn oil used with potatoes , falafel and eggplant. Deep-frying proved the best process used with eggplant. The percent loss in pesticide residues in contaminated oil without using in frying ,reached 89.20 , 71.25, 77.50 and 88.00% in case of γ-BHC (gamma benzene hexachloride) , heptachlor epoxide , endrin and p,p'-DDE{1,1'-(2,2-dichloroethenylidene)-bis(4-chlorobenzene)} ,respectively.

LIST OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1. INTRODUCTION

The edible oil is an important foodstuff for the human diet and health which contributes significantly in the economics of some countries. A good example is in concern on what happened in Malaysia, where the application of modern technologies in the extraction, purification and production of edible palm oil, putting the national economy of Malaysia among the developed countries **(Ling-Zhi *et al.*, 2007)**.

Egypt, like many developed countries suffered from inadequate local oil production and resort to the completion of its need through import. Oil industry in Egypt facing many of the obstacles, which eventually lead to a shortage in the domestic oil production as well as inadequate to meet the needs and requirements of Egyptian consumers.

The most important chemical standard specifications that determine the validity of oil for human consumption are acid value, saponification value, esterification value, iodine value and peroxide value **(AOAC International, 1997)**. To achieve these specifications of edible oils we must be stressed and control their quality and purity. Also, we have to ensure that oil is free of chemical impurities, including pesticide residues especially organochlorine pesticides.

Saitta, (2000) reported the impact of organochlorine pesticide residues on liver, where it breaks down its function and accompanied by cirrhosis and liver damage. Pesticides also have an adverse effect on the nervous system as it leads to the inability of mind and joint pain, fatigue muscular and nervous tension deep, headache and bone pain.

Organochlorine pesticides has its direct and adverse effects on a women's uterus , the chilling effect of some hormones, the pituitary gland and the ability to damage the kidneys , the occurrence of serious damage to the brain and nerves, and an effects last between memory loss and

insomnia (**Stanley, 1995)**. As these pesticides are stored in the brain and nerves, these have an indirect role in the formation of cancers and reduce supply of the body with Vitamin B **(Zahm and Ward 1998)**.

Pinero-Gonzalez *et al.,* (2007) reported that organochlorine pesticide residues (OCPs): hexachlorobenzene (HCB), lindane, cis-chlordane, heptachlor, aldrin, dieldrin, endrin and o,p'-DDT were found in vegetable oils of corn, soybean, sunflower and mixtures of oils in Venezuela.

The role of frying processes on edible oils characteristics were stated by **(Xiuzhu *et al.,* 2011)**. They found that frying processes caused increasing effects on acid and peroxide values, while the contrary was occurred with iodine and saponification values than unfried ones.

The effects of frying processes and adsorbents on the characteristics and removal of OCPs from edible oils were reported by **Zahangir *et al.,* (2007)**. They found that activated charcoal as adsorbent was effective in removing pesticide residues.

The present investigation aimed to:

- Monitoring and minimizing the types and quantities of the organochlorine pesticide residues in samples of edible oils collected from markets of Cairo governorate.
- Studying the role of shallow and deep frying of corn oil spiked with known amounts of organochlorine pesticides on their degradation.
- Studying the possibility of minimizing of organochlorine pesticide residues from spiked oil by using activated charcoal.

2. REVIEW OF LITERATURE

2.1. Oil Chemical Composition:

Yilmaz, (2004) developed the oil dilution technique and it saved oil (maize oil) expenditure in doughnut frying by approximately 30% without any compromise in doughnut quality, compared with standard small-scale control frying. Doughnut quality as evaluated by a sensory panel and absorbed fat content measurements also supported the main findings. In addition, either the oil density, acid value or alkaline contaminant materials can be effectively used to monitor oil quality changes during frying.

Karabulut *et al.*, (2004) formulated the fat/oil blends by mixing fully hydrogenated palm oil stearin or palm oil stearin with vegetable oils (canola oil and cottonseed oil) in different ratios from 30:70 to 70:30 (w/w %), were subjected to chemical interesterification reactions on a laboratory scale. Fatty acid (FA) composition, iodine value, slip melting point (SMP) and solid fat content (SFC) of the starting blends were analysed and compared with those of the interesterified blends. SMPs of interesterified blends were decreased compared to starting blends because of extensive rearrangement of FAs among triacylglycerols. These changes in SMP were reflected in the SFCs of the blends after the interesterification. SFCs of the interesterified blends also decreased with respect to the starting blends, and the interesterified products were softer than starting blends. These interesterified blends can be used as an alternative to partial hydrogenation to produce a plastic fat phase that is suitable for the manufacture of margarines, shortenings and confectionary fats.

Nik *et al.,* (2005) studied the thermal stability of palm oil as energy transport media in a hydraulic system. The oils were aged by circulating the oil in an open loop hydraulic system at an isothermal condition of 55^0C for 600 hrs. The thermal behavior and kinetic parameters of fresh and degraded palm oil, with and without oxidation inhibitor, were studied using the dynamic heating rate mode of a thermogravimetric analyser (TGA). Viscometric properties, total acid number and iodine value analyses were used to complement the TGA data. The thermodynamic parameter of activation energy of the samples was determined by direct Arrhenius plot and integral methods. The results may have important applications in the development of palm oil based hydraulic fluid. The results were compared with commercial vegetable based hydraulic fluid. The use of F10 and L135 additives was found to suppress significantly the increase of acid level and viscosity of the fluid.

The antioxidant properties of the essential oils of *Thymbra capitata*, *Thymus mastichina* and *T. camphoratus* collected during the vegetative phase (January 2002) at Algarve, Portugal, were evaluated and compared to synthetic antioxidants (butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT)) by **Miguel *et al.,* (2005)**. In addition, the chemical composition of the essential oils was determined using gas chromatography and gas chromatography-mass spectrometry. Antioxidant activity was measured by determination of the free radical scavenging activity of the essential oils in groundnut and sunflower oils. Results revealed that the essential oils were predominantly composed of oxygen-containing monoterpenes (61-76%). Carvacrol was the dominant component in *Thymbra capitata* oil (72%), 1,8-cineole (49%) in Thymus mastichina oil, and linalool (17%), linalyl acetate (15%) and 1,8-cineole (11%) in *T. camphoratus* oil. The essential oils and BHA showed weak