

# MODELLING OF PESTICIDE UPTAKE IN PLANTS

Ahsan Munir

A Thesis Submitted in Partial Fulfilment of the Requirements  
for the Degree of Master of Science  
The Petroleum and Petrochemical College, Chulalongkorn University  
in Academic Partnership with  
The University of Michigan, The University of Oklahoma,  
Case Western Reserve University and Institut Français du Pétrole

2005

ISBN 974-9937-08-2

I 229A7612

**Thesis Title:** Modeling of Pesticide Uptake in Plants  
**By:** Ahsan Munir  
**Program:** Petrochemical Technology  
**Thesis Advisors:** Asst. Prof. Kitipat Siemanond  
Prof. Rafiqul Gani

---

Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.

*Nantaya Yanumet*  
..... College Director  
(Assoc. Prof. Nantaya Yanumet)

**Thesis Committee:**

*Kitipat Siemanond*  
.....  
(Asst. Prof. Kitipat Siemanond )

*Rafiqul Gani*  
.....  
(Prof. Rafiqul Gani)

*Chintana Saiwan*  
.....  
(Assoc. Prof. Chintana Saiwan)

*Pomthong Malakul*  
.....  
(Asst. Prof. Pomthong Malakul)

## ABSTRACT

4671027063: Petrochemical Technology Program  
Ahsan Munir: Modelling of Pesticide Uptake in Plants.  
Thesis Advisors: Asst.Prof. Kitipat Siemanond  
and Prof. Rafiqul Gani pp. 84 ISBN 974-9937-08-2

Keywords: Pesticide / Formulation/ Computer-aided tools/ Uptake model

The design of Pesticide formulation through a set of computer aided method and tools are discussed in this work relative to the physical properties of an array of pesticides. Computer-aided tools can be used for the selection of the formulation type, for processing and for formulation design. Also, the appropriate selection tools can enhance or simplify the process of ingredient optimization.

A suite of computer-aided tools based on the systematic methods for pesticide formulation design and analysis has been developed. These tools have been integrated into a framework that allows rapid and efficient access to the needed data, to the needed property and performance models and to the synthesis/design algorithms that generate and evaluate formulated product alternatives. The tools include property models for complex molecules and their solutions (including polymers and surfactants), multistage performance models (uptake, release models), algorithms for molecule and mixture design, database of knowledge (plants, pesticides, etc.), and guidelines for problem solution strategies.

The main aim of this project is to develop Pesticide uptake model with the database of plants, pesticide and surfactants, which can be integrated into the framework for efficient formulation design. The use of framework and its tools is highlighted through a practical case study where several feasible formulation alternatives were generated in an effective manner.

Therefore, through the use of framework and its tools, it will be possible to achieve the objective of fast evaluation of products, reduction of time to market and reduction of cost of the product. That is, convert molecules to money.

## บทคัดย่อ

อาชาน มูเนอร์ : แบบจำลองการเกาะตัวของยาฆ่าแมลงบนใบไม้  
(Modeling of Pesticide Uptake in Plants)

อ. ที่ปรึกษา: ผศ.ดร. กิติพัฒน์ สีมานนท์ ศ.ดร. มิเกล บากาเฮวิช xxx หน้า ISBN 974-9937-08-2

การออกแบบสูตรยาฆ่าแมลงด้วยวิธีการทางคอมพิวเตอร์คืองานวิจัยที่ต้องใช้คุณสมบัติทางกายภาพของลำดับชนิดยาฆ่าแมลงซึ่งจะช่วยในการคัดเลือกชนิดยาฆ่าแมลงที่เหมาะสม การออกแบบยาฆ่าแมลงได้ถูกพัฒนาขึ้นโดยรวมเข้ากับโครงสร้างของฐานข้อมูลที่เป็นคุณสมบัติ แบบจำลอง และขั้นตอนการผลิตและเลือกชนิดยาฆ่าแมลงได้อย่างแม่นยำและรวดเร็ว แบบจำลองนี้ประกอบด้วย แบบจำลองคุณสมบัติสำหรับ โมเลกุลเชิงซ้อน พอลิเมอร์ กับ สารลดแรงตึงผิว แบบจำลองการเกาะตัวของยาฆ่าแมลงในหลายระดับ ขั้นตอนการออกแบบ โมเลกุลกับของผสม ข้อมูลชนิดยาฆ่าแมลงกับพืช และ แนวทางในการแก้ไขปัญหา เป้าหมายหลักของงานวิจัยนี้ คือ การพัฒนาแบบจำลองการเกาะตัวของยาฆ่าแมลง ซึ่งได้ถูกทดสอบกับกรณีศึกษาจริง และ ให้ผลของสูตรยาฆ่าแมลงหลายแบบ ที่เหมาะสมกับชนิดพืชนั้นๆ โดยสรุป แบบจำลองนี้สามารถช่วยประเมินคุณภาพยาฆ่าแมลง และราคา ยาฆ่าแมลงถูกลง และ ออกสู่ตลาดได้เร็วขึ้น

## ACKNOWLEDGEMENTS

First and foremost, my sincere thanks are due to Professor Rafiqul Gani who has provided me a chance to work at CAPEC, DTU, Denmark. It had been a wonderful exposure that has benefited me a lot. I am especially grateful for his excellent guidance, patient hearings and long sessions of discussions, which were of great help to me for completing this project on time.

I feel a great sense of gratitude to Dr. Gordon Bell, Syngenta, UK who has provided me with all possible information and guidance when and where required.

I am indebted to my Professor at home institution, Assistant Professor Kitipat Siemanond, Chulalongkorn University, Thailand, for providing me required help and co-operation.

I am grateful for the partial scholarship and partial funding of the thesis work provided by Postgraduate Education and Research Programs in Petroleum and Petrochemical Technology (PPT Consortium).

I express my sincere thanks to Jan Kamyno Rasmussen and Mauricio Sales-Cruz, Ph.D students and all the other CAPEC workers who have helped me directly or indirectly whenever I needed.

Last but not the least, heartfelt thanks are due to my family and friends, specially my parents who have left no stone unturned in every aspect.

## TABLE OF CONTENTS

	<b>PAGE</b>
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	viii
List of Figures	x
Notations	xii
 <b>CHAPTER</b>	
<b>I INTRODUCTION</b>	<b>1</b>
1.1 Chemistry & Technology of Agrochemical Formulation	2
1.2 Formulations of Agrochemicals	7
<b>II FRAMEWORK FOR FORMULATION DESIGN</b>	<b>11</b>
<b>III LITERATURE REVIEW</b>	<b>23</b>
3.1 Background Theory	23
3.2 Pesticide Solutions	25
3.3 Pesticide properties	26
3.4 Surfactant Properties	27
<b>IV PESTICIDE UPTAKE MODEL</b>	<b>29</b>
4.1 Model Description	29
4.1.1 Droplet Evaporation Model	32
4.1.2 Mass Balances	37
4.1.3 Uptake Definition	49

<b>CHAPTER</b>		<b>PAGE</b>
<b>V</b>	<b>RESULTS AND DISCUSSIONS</b>	<b>51</b>
	5.1 Model Development and Validation	51
	5.2 Uptake Models	
	5.2.1 Version 1	56
	5.2.2 Version 2	59
	5.2.3 Version 3	60
	5.2.4 Final Version	62
	5.3 Pesticide Formulation Design: Case Studies	68
	5.3.1 Case study 1: Cyanazine	69
	5.3.2 Case Study 2: Phenyl Urea	72
<b>VI</b>	<b>CONCLUSIONS AND RECOMMENDATIONS</b>	<b>76</b>
	<b>REFERENCES</b>	<b>77</b>
	<b>APPENDICES</b>	<b>79</b>
	<b>Appendix A: Simple COM – MoT (Excel Macro) Interface</b>	<b>79</b>
	<b>Appendix B: Structures of Active Ingredient and Surfactants</b>	<b>83</b>
	<b>CURRICULUM VITAE</b>	<b>85</b>

## LIST OF TABLES

TABLE	PAGE
1.1 Major types of pesticide formulations	9
2.1 Total Thickness of Cuticular Layer of different Plant Species.	12
2.2 Pesticides & their Properties.	13
2.3 Surfactants & their Properties.	14
2.4 Estimated Partition Coefficients for some Pesticides & Surfactants.	15
2.5 Logarithmic partition coefficients for surfactants.	15
2.6 Partition coefficients for surfactants.	16
2.7 McGowan Volume for Pesticides.	16
2.8 McGowan Volume for surfactants.	16
2.9 Calculated model parameters for four pesticides.	17
2.10 Calculated model parameters for surfactants.	18
2.11 Estimated contact angles and surface area of surfactants.	20
2.12 Property Estimation Tools and their functions.	21
5.1 Common Parameters.	52
5.2 Estimated Parameter values for Cyanazine needed in the model.	53
5.3 Estimated Solubility of Cyanazine in Water and ethoxy-surfactants.	53
5.4 Calculated initial concentrations of Cyanazine in droplet.	54
5.5 Partition coefficients for surfactants.	54
5.6 McGowan Volume for surfactants.	54
5.7 Calculated initial concentrations for surfactants.	55



<b>TABLE</b>	<b>PAGE</b>
5.8 Estimated contact angles and surface area of surfactants.	55
5.9 Additional parameter values for Diffusivity correlations.	57
5.10 Comparison of results of Model 1 and Model 2 with Experimental Data.	60
5.11 Fitted values of K3 for Uptake of Cyanazine at 24h and 120h.	61
5.12 Calculated solubility of cyanazine in different surfactants.	63
5.13 Initial droplet concentrations of cyanazine.	64
5.14 Predicted % Uptake of Cyanazine at 24h and 120h.	64
5.15 Fitted values of K4 for Uptake of Cyanazine at 24h and 120h	66
5.16 Percentage Uptake of Cyanazine at 24h and 120h	69
5.17 Percentage Uptake of Phenyl urea at 8h & 24h	73

## LIST OF FIGURES

FIGURE	PAGE
2.1 Framework for formulation design.	11
2.2 Diagrammatic Representation of Tools used in Formulation Design	21
3.1 Diagrammatic representation of various parts of leaf	23
4.1 Diagrammatic representation of scenario modeled.	29
4.2 Model scenario for evaporation of droplet	32
4.3 Droplet Volume (Vd) and Surface area (S) vs. time for evaporation of water	36
4.4 Scenario of droplet at times t1 and t2.	37
4.5 Scenario for Multilayer Model	40
4.6 Pesticide uptake: scenario modeled and equations.	49
5.1 Comparison of results for uptake of Cyanazine at 24 hours.	58
5.2 Sensitivity Analysis of Diffusivity Correlations	61
5.3 Sensitivity Analysis for new diffusivity correlation	65
5.4 Predicted Uptake vs. Experimental Uptake for Cyanazine at 24h(▲) and 120h(■)	67
5.5 Effects of ethylene oxide content and concentration of aliphatic alcohol surfactants on uptake of Cyanazine at 24hours after application to wheat plant. Dotted lines indicates uptake of the compound in absence of surfactants	70
5.6 Effects of ethylene oxide content and concentration of aliphatic alcohol surfactants on uptake of Cyanazine at 120 hours after application to wheat plant. Dotted lines indicates uptake of the compound in absence of surfactants.	70
5.7 Relative uptake of AI (Cyanazine) and adjuvant (C13E11) at 24 hours with surfactant concentration of 0.2 g/l.	71

<b>FIGURE</b>		<b>PAGE</b>
5.8	Relative uptake of AI (Cyanazine) and adjuvant (C13E11) at 24 hours with surfactant concentration of 1 g/l.	72
5.9	Effects of ethylene oxide content and concentration of aliphatic alcohol surfactants on uptake of Phenyl urea at 24hours after application to wheat plant.	74
5.10	Percentage Uptake of surfactants.	74

## NOTATIONS

$x_{wax}$  = wax thickness(m)

$x_{cut}$  = cuticle thickness (m)

$h_{wax}$  =Thickness of each layer in wax(m)

$h_{cut}$  =Thickness of each layer in cuticle(m)

$t$ =time in hours

$t_u$ =uptake time in hours

$t_f$ =time factor

$S$ =Surface area of droplet as a function of time ( $m^2$ )

$S_0$ =initial surface area of droplet

$S_f$ =surface factor

$v$ =Volume factor

$V_d$ =Droplet Volume as a function of time ( $m^3$ )

$V_0$ =initial volume of droplet ( $m^3$ )

$V_p$ = Volume of Plant

$EO$ =Number of Ethoxy unit in surfactant

$K_4$ =Tortuosity Factor

$SR$ =Surfactant rate (g/l)

$M_{adjtotal}$ =total moles of adjuvant in droplet (mol)

$M_{adj}$ =initial moles of solid adjuvant in droplet (mol)

$C_{dadj}$ =initial concentration of adjuvant in droplet ( $mol/m^3$ )

$C_{adj0}$ -  $C_{adj30}$ =concentration of adjuvant in 0 to 30 layer of wax and cuticle ( $mol/m^3$ )

$C_{padj}$ =concentration of adjuvant in plant ( $mol/m^3$ )

$K_{wdadj}$ =partition coefficient of adjuvant between droplet and wax

$K_{wcadj}$ = partition coefficient of adjuvant between wax and cuticle

$K_{cpadj}$ = partition coefficient of adjuvant between cuticle and plant

$MV_{adj}$ =McGowan Volume of adjuvant ( $cm^3/mol$ )

$MW_{adj}$ =Molecular weight of adjuvant

$\rho_{oadj}$ =Density of adjuvant ( $g/cm^3$ )

$D_{adjwax0}$  -  $D_{adjwax15}$  = Diffusivity of adjuvant in wax layers ( $m^2/s$ )

$D_{ajcut}$  = Diffusivity of adjuvant in cuticle ( $m^2/s$ )

$\rho_{wax}$  = density of wax ( $kg/m^3$ )

$MAI_{total}$  = total moles of active ingredient in droplet (mol)

$MAI$  = initial moles of solid active ingredient in droplet (mol)

$C_{dAI}$  = initial concentration of active ingredient in droplet ( $mol/m^3$ )

$C_0 - C_0$  = concentration of active ingredient in 0 to 30 layer of wax and cuticle ( $mol/m^3$ )

$C_{pAI}$  = concentration of active ingredient in plant ( $mol/m^3$ )

$K_{wdAI}$  = partition coefficient of active ingredient between droplet and wax

$K_{wcAI}$  = partition coefficient of active ingredient between wax and cuticle

$K_{cpAI}$  = partition coefficient of active ingredient between cuticle and plant

$MVAI$  = McGowan Volume of active ingredient ( $cm^3/mol$ )

$MWAI$  = Molecular weight of active ingredient

$DAI_{wax0}$  -  $DAI_{wax15}$  = Diffusivity of active ingredient in wax layers ( $m^2/s$ )

$DAI_{cut}$  = Diffusivity of active ingredient in cuticle ( $m^2/s$ )

$S_{adj}$  = solubility of active ingredient in adjuvant (g/l)

$S_{water}$  = solubility of active ingredient in water (g/l)

$RelUptAI_{tot}$  = Total relative uptake of active ingredient

$RelUptadj_{tot}$  = Total relative uptake of adjuvant