DEVELOPMENT OF SURFACE COATING MATERIALS OF WAX ESTERS AND EPOXIDES FOR COATING INDUSTRIES

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By

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DEVELOPMENT OF SURFACE COATING MATERIALS OF WAX ESTERS AND EPOXIDES FOR COATING INDUSTRIES

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There has been an increasing interest and strong demand for fine quality coating materials that can be applied to various substrates. Coating materials contained high proportion of acrylate based products which affect human health related toxicity, primarily on carcinogenicity. Researchers make efforts to eliminate this substrate by replacing with other materials such as wax esters and epoxides from renewable raw materials especially oil crops. A major problem with this kind of application is, coating characteristics features are very low, thus ingredient of coating formulation was developed to improve coating characteristics.

In this research, two different model reactions and an end application of coating formulation were studied. Firstly, esters were produced as reactive diluents in coating component through enzymatic esterification of fatty acids, and secondly, chemo-enzymatic epoxidations were carried out to produce epoxidized fatty acids. Finally, both products were formulated to be used in coating formulation.

Enzymatic syntheses of esters from oleochemicals and petrochemicals were studied using Novozyme 435 as biocatalyst. Immobilized enzyme was utilized due to their considerable advantages over enzymes in bulk solution such as high thermal and operational stability as well as easy recovery. Results showed that Novozyme 435 is a good biocatalyst in esterification of esters with high percentage of yield of more than 95.0%. The optimum conditions for esterification of adipate esters were 30 minutes incubation period, while it was carried out at 50°C, and hexane as a solvent.

Chemo-enzymatic epoxidation of fatty acids which are oleic acid, linoleic acid and ricinoleic acid was also catalyzed by Novozyme 435 and hydrogen peroxide; in a solvent-free medium. Immobilized enzyme was used to catalyze the formation of peracid from fatty acid, meanwhile hydrogen peroxide was utilized for the epoxidation of the vinyl group of fatty acids to form the desired epoxide. Synthesis of epoxidized oleyl oleate by oleic acid and oleyl alcohol gave 3.7 oxirane number and 94% yield. Reaction of linoleic acid and oleyl alcohol produced 92% of epoxidized linoleyl oleate with 2.7

oxirane number. Yield (89%) of epoxidized ricinoleyl oleate was produced by the reaction of ricinoleic acid and oleyl alcohol with 1.8 oxirane number.

Wax esters and epoxides were applied as surface coating formulation containing adipate esters, fatty acid epoxides, epoxy acrylate, Brij 30, PETIA and photoinitiator and dried by UV radiation curing. Coated film from this formulation gave good performance during Soxhlet extraction and hardness test. In this study, gel content exhibited more than 90.0% polymerization, while the pendulum hardness gave 55.3% of hardness. Both analyses were significant to determine the effect of irradiation passes. Scratch test was carried out to verify the resistant of coating. The highest weight loaded can be resisted by the wax esters formulation was 4.5 N.

In order to produce high quality coating formulation, screening of compositions of epoxy acrylate was done to reduce the toxicity percentage. Samples were formulated containing epoxy acrylates and epoxides from epoxidized soybean oil (ESBO) and fatty esters. Both formulations were used to improvise the properties of coating by replacing acrylate with epoxides and wax esters. In evaluation of coating performance, epoxy acrylate was reduced until 75% composition with high quality coatings formulation (Formulation 23-24).

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PEMBANGUNAN BAHAN PENYALUTAN PERMUKAAN DARIPADA ESTER LILIN DAN EPOKSIDA UNTUK INDUSTRI PENYALUTAN

Oleh

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Terdapat peningkatan terhadap minat dan permintaan tinggi untuk bahan penyalutan yang berkualiti bagi aplikasi ke atas pelbagai bahan. Bahan penyalutan mengandungi nisbah produk yang tinggi berasaskan akrilat, mempengaruhi kesihatan manusia yang berkaitan dengan ketoksikan, terutamanya karsinogenan. Penyelidik berusaha untuk menghapuskan bahan ini dengan menggantikannya dengan bahan lain seperti ester lilin dan epoksida daripada bahan mentah yang boleh diperbaharui terutama sekali tanaman berasaskan minyak. Masalah besar yang dihadapi dengan aplikasi ini, ialah ciri penyalutan yang sangat rendah, justeru itu bahan formulasi penyalutan perlu dibangunkan untuk memperbaiki ciri penyalutan.

Dalam penyelidikan ini, dua model tindakbalas yang berbeza dan satu aplikasi akhir formulasi penyalutan dikaji. Pertama, ester dihasilkan sebagai pelarut reaktif dalam komponen melalui pengesteran asid lemak. Kedua, pengepoksidaan kemo-berenzim dijalankan untuk menghasilkan asid lemak terepoksida. Akhir sekali, kedua-dua hasil ini diformulasi untuk digunakan dalam formulasi penyalutan.

Sintesis berenzim ester daripada produk oleokimia dan petrokimia dikaji dengan menggunakan Novozyme 435 sebagai pemangkin. Enzim tersekatgerak lipase telah diaplikasikan sebagai biomangkin berdasarkan kepada kelebihan enzim ini dalam larutan berkuantiti besar, seperti tekanan terma yang tinggi dan kestabilan pengendalian serta mudah untuk diperolehi semula. Keputusan menunjukkan Novozyme 435 merupakan enzim yang baik untuk pengesteran asid adipik dengan peratusan hasil yang tinggi lebih daripada 95.0%. Keadaan optimum yang digunakan untuk pengesteran ester adipat adalah masa tindak-balas 30 minit, pada suhu 50°C dan heksana sebagai pelarut.

Pengepoksidaan kemo-berenzim untuk asid lemak iaitu asid oleik, asid linoleik dan asid risinoleik juga bermangkinkan Novozyme 435 dan hidrogen peroksida; tanpa pelarut. Enzim tersekatgerak digunakan untuk memangkinkan pembentukan perasid daripada asid lemak dan hidrogen peroksida, yang digunakan untuk pengepoksidaan kumpulan vinil untuk menghasilkan epoksida yang diperlukan. Sintesis oleil oleat terepoksida

daripada asid oleik dan alkohol oleil memberikan 3.7 nombor oksiran dan 94% hasil. Tindakbalas asid linoleik dan alkohol oleil menghasilkan 92% linoleil oleat terepoksida dengan 2.7 nombor oksiran. Risinoleil oleat (89%) terhasil daripada tindakbalas asid risinoleik dan alkohol oleil dengan 1.8 nombor oksiran.

Ester lilin dan epoksida diaplikasi sebagai formulasi penyalutan permukaan yang mengandungi ester adipat, epoksida asid lemak, epoksi akrilat, Brij 30, PETIA dan bahan pemula dikeringkan dengan menggunakan teknologi radiasi UV. Salutan filem daripada formulasi ini memberikan prestasi yang baik semasa pengestrakan Soxhlet dan ujian ketahanan. Dalam kajian ini, kandungan gel menunjukkan lebih daripada 90.0% pempolimeran, manakala ujian ketahanan memberikan 55.3%. Kedua-dua analisis ini adalah penting untuk menentukan kesan bilangan dedahan radiasi. Ujian calaran dilakukan untuk memastikan ketahanan salutan. Beban yang paling tinggi yang boleh ditampan oleh formulasi ester lilin adalah 4.5 N.

Bagi menghasilkan formulasi penyalutan yang berkualiti tinggi, penyaringan terhadap komposisi epoksi akrilat dilakukan untuk mengurangkan peratusannya. Sampel diformulasi sama ada mengandungi epoksida minyak kacang soya atau ester lemak. Kedua-dua formulasi ini dilakukan untuk memperbaiki kriteria penyalutan bagi menggantikan akrilat dengan epoksida dan ester lilin. Dalam penilaian prestasi penyalutan, epoksi akrilat

dikurangkan sehingga 75.0% komposisi dengan menghasilkan formulasi penyalutan berkualiti tinggi (Formulasi 23-24).

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I certify that a Thesis Examination Committee has met on ……. to conduct the final examination of Noraini Binti Abd Ghani on her Doctor of Philosophy thesis entitled "Development of Surface Coating Materials of Wax Esters and Epoxides for Coating Industries" in accordance with the Universities and University College Act 1971 and the Constitution of the Universiti Pertanian Malaysia [P.U.(A) 106] 15 March 1998. The committee recommends that the student be awarded the degree of Doctor of Philosophy, PhD.

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been acknowledged. I also declare that is has not been previously and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

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NORAINI BINTI ABD GHANI

Date: 24 July 2012

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEME

LIST OF ABBREVIATIONS

GC-MS	Gas Chromatography-Mass Spectroscopy
FT-IR	Fourier Transform- Infrared Spectroscopy
TLC	Thin Layer Chromatography
VOCs	Volatile Organic Compounds
HAPs	Hazardous Air Pollutants
UV	Ultraviolet
EB	Electron Beam
SEM	Scanning Electron Microscopy

CHAPTER 1

INTRODUCTION

1.1 Background of Research

Wooden materials can be protected from adverse factors such as visible light, UV-light, oxygen, heat, humidity and water, biological attack and air pollutants, using various protective and decorative finishes such as paints, transparent stains and penetrating finishes or film forming clear varnishes (Pascal *et al*., 2003). Interest and demand for transparent systems which protect as well as show the aesthetic features of wood (color and texture) has always been increasing.

Industrial sectors are developing future coatings technology to improve solvent based products to environmental friendly systems to meet consumer demand. There is high awareness in the synthesis of waxes to serve as ingredients in coatings for wooden surfaces, which contribute to minimum pollutants and with substrates from renewable resources (Nordblad *et al*., 2009). The usage of wax esters is attractive as they are non-hazardous compounds with good

biodegradability. Thus, wax esters have great potential in replacing solvent as carrier in formulation of ingredients for surface coating.

Conventional extractions from plant materials and direct biosynthesis by fermentation are the two methods for organic esters synthesis. However, these methods exhibit high cost of processing and low yields of desired esters and therefore, better processes need to be developed to serve as the environmental benign processes. Chemical routes normally problems such as poor reaction selectivity and extreme reaction condition leading to undesirable side reactions, low yields, pollution and high cost of manufacturing.

Previously, traditional chemical epoxidation method with peracetic or performic acid were used to oxidize the unsaturated bonds to form epoxy rings (Swern, 1947). The main drawback with chemical method is the acid-catalyzed side-reaction of ring-opening, resulting in several by-products (Ikhuoria *et al*., 2007). This conventional method was replaced by chemo-enzymatic epoxidation as an alternative, which peracid is usually formed in-situ by hydrogen peroxide (French, 1971).

Most of today's commercial enzymatic processes have a variety of positive characteristics, such as high productivity and a lack of undesirable by-product. As an alternative, the use of lipases to catalyze these synthesis reactions has

recently become a much more promising method (Rejasse *et al*., 2003), as a green and environmentally benign process. Lipase catalysis offers greenness and more energy-efficient means of production than chemical processes, leading to fewer by-products, simpler product recovery and less waste generation (Tornvall and Hatti-Kaul, 2007).

Lipase-catalyzed reactions are superior to conventional chemical methods owing to high catalytic efficiency and the inherent selectivity of the natural catalysts which results in much purer products with greater rapidity under mild reaction conditions (Hasan *et al*., 2006). In recent years, enzyme catalyzed reaction has been widely understood and able to produce high purity product at mild temperature and atmospheric pressure (Chaibakhsh *et al*., 2009; Abdul Rahman *et al*., 2004).

In this work, studies were carried out as follows; (1) production of high yield esters as reactive diluents in coating formulation, (2) production of epoxides as formulation's ingredient through chemo-enzymatic epoxidation, and (3) formulation and application of coating ingredients. Pure lipase from *Candida rugosa* and immobilized lipases (Novozyme 435 and Lipozyme RM IM) were screened to obtain suitable catalyst. Novozyme 435 was selected to catalyze esterification of wax esters based on preliminary result. In chemo-enzymatic epoxidation reaction, Novozyme 435 was used to catalyze formation of peracid

from fatty acid and hydrogen peroxide (*in situ*) for the epoxidation of the carbon-carbon double bond to form the desired epoxide. Wax esters and epoxides were utilized as reactive diluents in coating formulations.

1.2 Problem Statements

Surface coating is meant to have bi-functional purposes, as protection and decoration. Formulations of surface coatings with UV curable technology are used worldwide. In Malaysia, wood coatings market comprises mainly of nitrocellulose based coatings, acid cured and polyurethane coatings. In order to achieve export earnings, furniture industries need to alternate from the mass market into designed products for targeted niche market (Al- Mahdi *et al*., 2007). The UV curable technology will increase the quota of high value-added products for exportation. However, until now, there is no local production of UV curable wood coating.

Rising concern for more environmentally benign products initiates the development for substitution of acrylate esters and solventless formulation. Acrylate esters have been known as hazardous substances could correlate to toxic effects, such as skin sensitization, mutagenicity and carcinogenicity, respiratory allergy, organ toxicity and necrosis (Aptula *et al*, 2006; Chan *et al*.,

2007). Even though organic solvents offer several advantages in enzymatic reactions and coating formulations, their usage in industrial processes are undesirable. Utilization of organic solvents requires expensive post-treatments actions, larger reactors, auxiliary equipments and inhibition effects on the enzyme (Tufvesson *et al*., 2007). The main disadvantage with organic solvents in coating formulations is they release volatile organic compounds (VOCs) to the atmosphere that can affect the environment via greenhouse effect and human health (Garcia and Suay, 2007; Stropp *et al*., 2006).

1.3 Objectives

The objectives of this research are to:

1) Synthesize wax esters (C30-C42) and epoxide esters using immobilized enzyme by esterification and chemo-enzymatic epoxidation.
2) Formulate adipate wax esters and epoxides as ingredients in coatings for wooden surfaces with solventless system.
3) Study the effect of irradiation doses to the hardness and gel content of coated surface.
4) Evaluate the performance of adipate wax esters and epoxides as surface coatings by mechanical properties tests.

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APPENDICES

1. "Development of Coating Materials from Liquid Wax Esters for Wood Top-Based Coating" *Journal of Coatings Technology and Research* Volume 8, Issue 2 (2010), Page 229-236.

2. Invention : Formulation for Coating Material
   United States Patent No. 8,057,588 B2 (November 15th 2011)
   International Patent Application No. PCT/MY2008/000094 (3rd September 2008)
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   Malaysian Patent Application No P1 20072080 (23rd November 2007)

3. Invention : A Method for Producing Adipate Ester
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5. Thin Layer Chromatograms

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(54) Title: A METHOD FOR PRODUCING ADIPATE ESTER

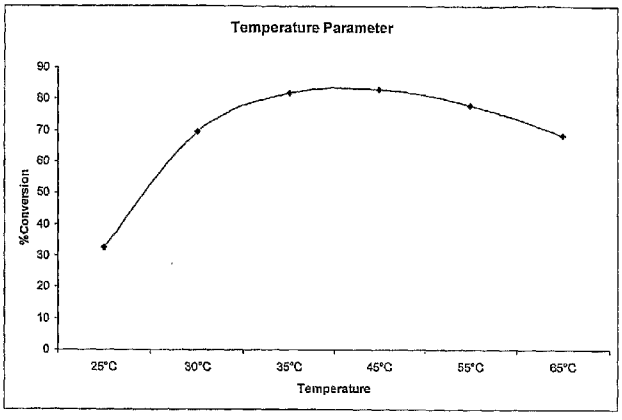

Figure 1: Percentage conversion of adipic acid and alcohol in various temperatures.

(57) Abstract: The present invention provides a method of producing a purified wax adipate ester comprising the steps of: (a) mixing adipic acid with an alcohol, (b) adding a highly stable biocatalyst such as an immobilized enzyme to form a homologous mixture, (c) incubating the mixture and (d) obtaining a purified adipate ester. The method further comprises optimization using Response Surface Methodology (RSM). Preferred enzymes include *Candida rugosa, Rhizomucor miehei* (Lipozyme RM IM), and *Candida antartica* (Novozym 435).

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A METHOD FOR PRODUCING ADIPATE ESTER

FIELD OF INVENTION

The present invention relates to the development of a highly stable biocatalyst such as immobilized enzyme for the synthesis of high added-value esters. More particularly, the present invention provides a process for producing wax ester, preferbally adipate esters.

BACKGROUND OF THE INVENTION

Adipate esters which are derived from compounds of C6 straight-chain dicarboxylic adipic acid and alcohol are of considerable industrial interest compared with the ordinary esters especially in petrochemical industries. The excellent properties of adipic esters such as its low toxicity, good thermal stability, low volatility and high biodegradability make it a very useful compound and significant to many industrial applications especially in domestic, health care products, and lubricant industries.

Adipate esters are produced by reacting an adipic acid and an alcohol at high temperatures in the presence of metal or chemical catalysts. This method leads to undesirable side reactions and degradation of esters. The use of those catalysts exposed to toxicity and corrosion. Reaction with homogenous chemical catalysts are usually time consuming and also give relatively low yields. Esterification reaction is a reversible process; hence the long time reaction may result in hydrolysis reaction.

At the present, the use of homogenous chemical catalysts for producing adipate esters may lead to several problems such as separation of products, hazards in handling of the corrosive acids, high energy consumption and degradation of esters. Thus, interests have grown on the use of green synthesis of esters in organic medium catalyzed by using immobilized enzyme.

However, for future industrial scale enzymatic production of adipate esters, it would be beneficial to simplify the reaction conditions as much as possible. Recently, optimization of enzyme-catalyzed production of various esters by Response Surface Methodology (which is an efficient statistical technique for optimization of multiple variables) and Artificial Neural Network (which estimates the response based on the trained data) has been investigated.

SUMMARY OF THE INVENTION

Accordingly, the object of the invention relates to a method of producing purified wax adipate ester. The method includes the steps of; mixing adipic acid with alcohol to obtain a mixture, adding a solution of enzyme into the mixture, shaking the mixture to form a homologous mixture, incubating the mixture for at least 2 hours, obtaining a product containing purified adipate ester; calculating percentage of the adipate ester;

Further to that, the mixture is incubated between 30 °C and 70 °C and the enzyme consists of immobilized lipases. The immobilized lipases that is preferred includes *Candida rugosa, Rhizomucor miehei* (Lipozyme RM IM), and *Candida antartica* (Novozym 435). Based on the method, the obtained product is adipate esters and the said product having at least a percentage between 35% and 90% of purified adipate ester(s). The method also further includes optimization using Response Surface Methodology (RSM), wherein the optimization produced a yield of at least 95% and above.

The Adipate esters which is produced from methods above having excellent properties of adipic esters such as its low toxicity, good thermal stability, low volatility and high biodegradability make it a very useful compound and significant to many industrial applications especially in domestic, health care products, and lubricant industries. The invention will be formulated as one of the ingredient in wood coating formulations.

Another application is as a plastic syringe which will be used in medical area because of its excellent properties. This invention was produced at mild conditions, which prevent degradation of starting materials and reduce side reactions. The use of immobilized enzyme has become a valid approach due to its special features which allow the reutilization of the enzyme and better separation of products. Furthermore, the percentage of yield is high and optimization was done using RSM which reduced number of experimental runs needed to provide sufficient information for statistically acceptable result.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 represents percentage conversion of adipic acid and alcohol in various temperatures.

Figure 2 represents the relative yield of the product obtained in various temperatures.

Figure 3 represents infrared spectrum of the adipate ester.

Figure 4 represents schematic diagram of artificial neural network (ANN)

Figure 5 represents mean squared error vs. epoch (cycle) during the training process

Figure 6 represents ANN correlation between the observed and predicted adipte ester yield.

Figure 7 represents response surface plot showing the effect of molar ratio, time and their interaction on the synthesis of adipate ester.

Figure 8 represents response surface plot showing the effect of temperature, reaction time and their interaction on the synthesis of adipate ester

BRIED DESCRIPTION OF THE INVENTION

The present invention discuss on the development of a highly stable biocatalyst such as immobilized enzyme for the synthesis of high added-value esters. The use of immobilized enzyme has become a valid approach due to its special features which allow the reutilization of the enzyme and better separation of products. Application of lipases in various biochemical modifications of fats and oils is well established, several dicarboxylic adipate esters produced in the present invention are useful as surfactants or chemicals additives. Accordingly, the object of the invention relates to a method for producing a high quality and purity wax adipate esters. In addition to that, the present invention also produces a high yield of adipate esters by esterification reaction of dicarboxylic acid preferably adipic acid with at least one alcohol in the presence of lipase. Further to this, the invention describes in detail on an improve method to carry out the above method on large-scale basis to produce a product such as adipate ester(s). The product is optimized by using RSM/ANN.Further to the method, the present invention related to a method for producing adipate ester by enzymatically esterifiying dicarboxylic acid preferably adipic acid with at least one alcohol which contains 2 to 18 carbons per molecule. In the preferred embodiment of the present invention, the adipic acid is derived from cyclohexane. In another embodiment of the present invention the adipic acid may be derived from other petrochemical–based compounds. The alcohol used in the present invention can be linear or branched alcohol contains 2 to 18 carbons per molecule.Adipate ester(s) is developed by mixing adipic acid and alcohol in a shaker. A sutaible mixture is obtain when adipic acid and alcohol is placed in a shaker and continuously shaking the shaker at temperature in the range from about 30 °C to 70 °C. Further to this, an esterification reaction is carried out with organic solvent as a medium and with enzyme as the biocatalyst. An immobilized lipase enzyme is chosen as a biocatalyst in the reaction mixture to facilitate the esterification reaction. The immobilized lipase is recycled with the selectivity of the immobilized lipase and purity of the product is controlled.

The effect of parameters on the reaction and their interaction on the production of ester is investigated by use of RSM, Central Composite Rotatable Design (CCRD). To train an ANN model a set of data containing inputs and outputs are fed. The same experimental data used in each RSM design is used as the training data of the ANN. The excellent properties of adipic esters such as its low toxicity, good thermal stability, low volatility and high biodegradability make it a very useful compound and significant to many industrial applications especially in domestic, health care products, and lubricant industries.

DETAILED DESCRIPTION OF THE INVENTION

The invention will now be described in more detail by reference to the following Figures and Examples. The following examples are provided for illustrative purposes only and are not intended to limit the invention.

According to the present invention, process for producing adipate ester comprises esterifying adipic acid compound with at least one alcohol in the presence of lipase as a catalyst and an organic solvent as the medium. In the preferred embodiment of the present invention, stated adipic acid is derived from petrochemical–based compounds whereas said alcohol is an alcohol with 2 to 18 carbon atoms per molecule.

Continuous shaking is applied to the reaction mixture and the mixture is allowed to proceed for 2 hours. Later, the reaction mixture is separated from the biocatalyst by filtration. The separated biocatalyst is then recycled and washed with organic solvent.

In the preferred embodiment of the present invention, the immobilized lipase is used. Immobilized lipase has the advantages by easy separation from the product and the reusability is allowed. Lipase is highly selective towards certain bonds and specific with respect to their substrates. Easy separation will permit efficient handling of the process while the reusability of lipase will allow for cost reduction and higher production.

The immobilize lipases that used in the present invention are *Candida antartica* (Novozym 435) or *Rhizomucor miehei* (Lipozyme RM IM). Both lipases are measured in the same amount if applied. The protein content of the mixture is controlled to maximize the adipate ester product.

In addition, it is preferred to use adipic acid compound derived from petrochemical–based cyclohexane.The ratio of adipic acid to alcohol is set to 1:2. In the preferred embodiment of the present invention, to get highest percentage conversion of adipic acid and alcohol to adipate ester, adipic acid and alcohol will be supplied at a mole ratio in the range of 1:1 to 1:6 with preferably 1:2 for short chain and 1:4 for medium chain length of alcohol used. The reaction is carried out in temperature with range from 30 °C to 70 °C with preferably 50 °C. In the present invention, the mixture undergoes continuous shaking in controlled temperature. Changing in the reaction temperature can be assigned to its effect on substrate solubility as well as its direct influences on the reaction rate, enzyme stability and activity.The percentage conversion is calculated based on the titration result compared with relative volume of substrate to product. In the present invention, the titration is performed after filtration of biocatalyst. NaOH neutralized the acidity of the reaction product until in excess to pH 10.

Adipate ester obtainable from the method according to the present invention is di(2-methyl-1-propyl) adipate which presented by formula (1):

(CH3)2CHCH2O2C(CH2)4CO2CH2CH(CH3)2 Formula 1

The present invention can be performed in various ways, but certain detailed routes embodying the present invention will be illustrated in the following examples.

EXAMPLE 1

A batchwise operation was carried out on a laboratory scale. Adipic acid (2.0 mmol) was weighed and placed in 6 sample vials each. Isobutanol (4.0 mmol) was added into the each vials followed by n-hexane (15.0 ml) as solvent. Then, lipase (0.3g) was added into three of the six vials and all vials were closed tightly. The reaction mixture of samples and control (sample without lipases) were incubated at 30 °C in a horizontal water bath shaker with shaking speed of 150 rpm continuously for 2 hours.

The reaction was terminated after 2 hours by diluting the sample with 3.5 ml of ethanol/acetone (1:1 vol / vol). The remaining free adipic acid in the reaction mixture was determined using a titration with 0.1M of NaOH until an end point of pH 10.0 which was detected by auto-titrator Metler-Toledo Metrohm equipment. The activity of lipase of each reaction was expressed as percentage of converted adipic acid. After that, the percentage of yield and relative yield were calculated.

The product has a relative yield about 88.36%. FT-IR: showed the sharp peak at 1736.00 cm-1 represented the existence of (C=O) bond for ester. The highest intensity for this peak strongly proved the presence of ester group in the compound. The presence of (C-O) bond in the compound was shown by the peak at 1176.00 cm-1 while the peak for alkyl groups were shown at 1464.00 cm-1 and 1378.00 cm-1, and the peak for alkanes was shown at 2960.00 cm-1.

EXAMPLE 2

Example 1 was repeated. The mixture was heated to 30°C in a water-bath shaker. The reaction was allowed to proceed for 1 h. The yield was about 39.16%.

EXAMPLE 3

Example 1 was repeated. The mixture without organic solvent was heated to 55 °C in a water-bath shaker. The reaction was allowed to proceed for 2 h. The yield is about 78.03%.

EXAMPLE 4

Fitting of the data to the various models (linear, two factorial, quadratic and cubic) and their subsequent analysis of variance (optimization study) showed that the synthesis of adipate ester was suitably described with quadratic polynomial model. The very small p-value (0.0001) and a suitable coefficient of determination, $R_2 = 0.9660$, showed that the quadratic polynomial model was highly significant and sufficient to present the actual relationship between the response and the significant variables.

CLAIMS

1. A method of producing purified wax adipate ester , wherein the method comprising the steps of:
    a) mixing adipic acid with alcohol to obtain a mixture,
    b) adding a solution of enzyme into the mixture from step (a)
    c) shaking the mixture from step (b) to form a homologous mixture;
    d) incubating the mixture from step (c) for at least 2 hours;
    e) obtaining a product containing purified adipate ester;
    f) calculating percentage of the adipate ester;

2. The method as claimed in claim1, wherein the mixture is incubated between 30 °C and 70 °C.

3. The method as claimed in claim1, wherein the enzyme consists of immobilized lipases.

4. The method as claimed in claim 3, wherein the immobilized lipases including *Candida rugosa, Rhizomucor miehei* (Lipozyme RM IM), and *Candida antartica* (Novozym 435).

6. The method as claimed in claim1, wherein the product obtained having at least a percentage between 35% and 90% of purified adipate ester.

7. The method as claimed in claim1 further includes optimization using Response Surface Methodology (RSM), wherein the optimization produced a yield at least 95% and above.

8. Adipate esters is produced from any of the preceding method claims 1 to 7.

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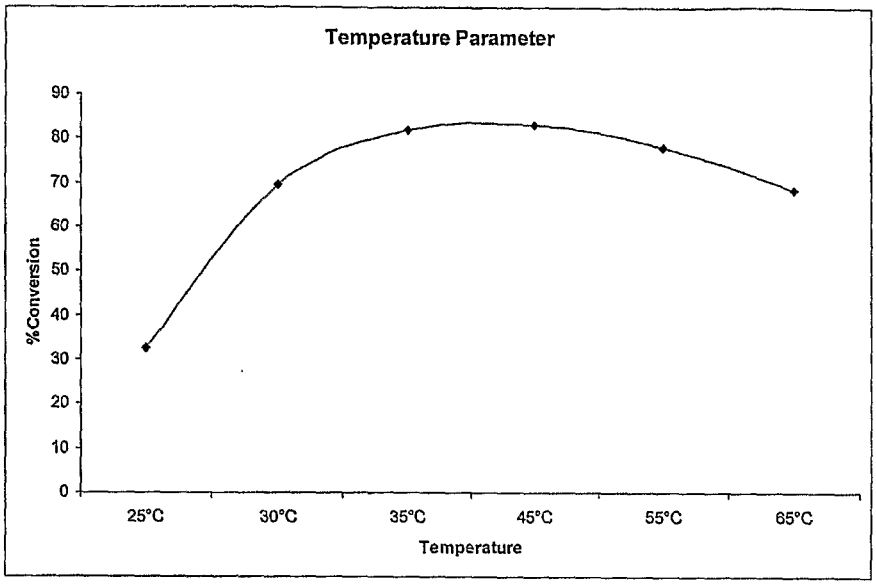


Figure 1: Percentage conversion of adipic acid and alcohol in various temperatures.

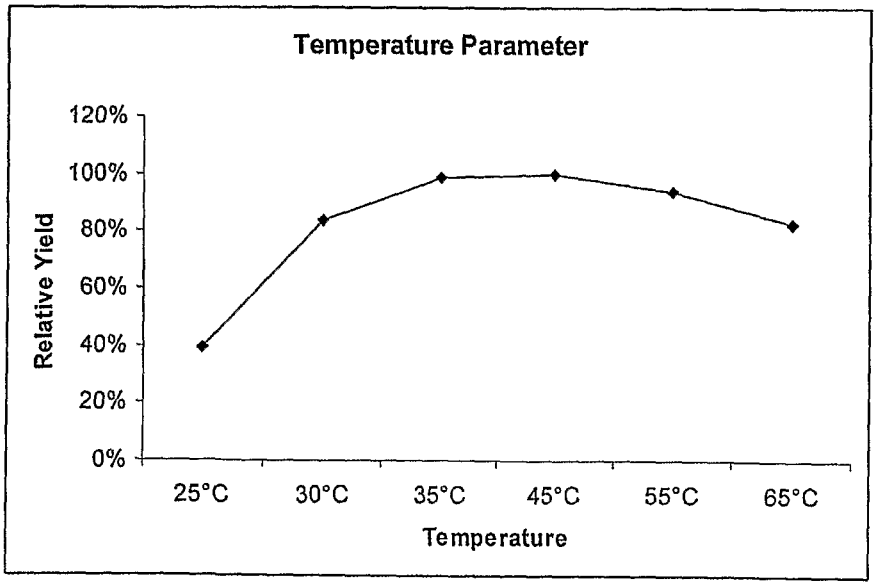


Figure 2: The relative yield of the product obtained in various temperatures.

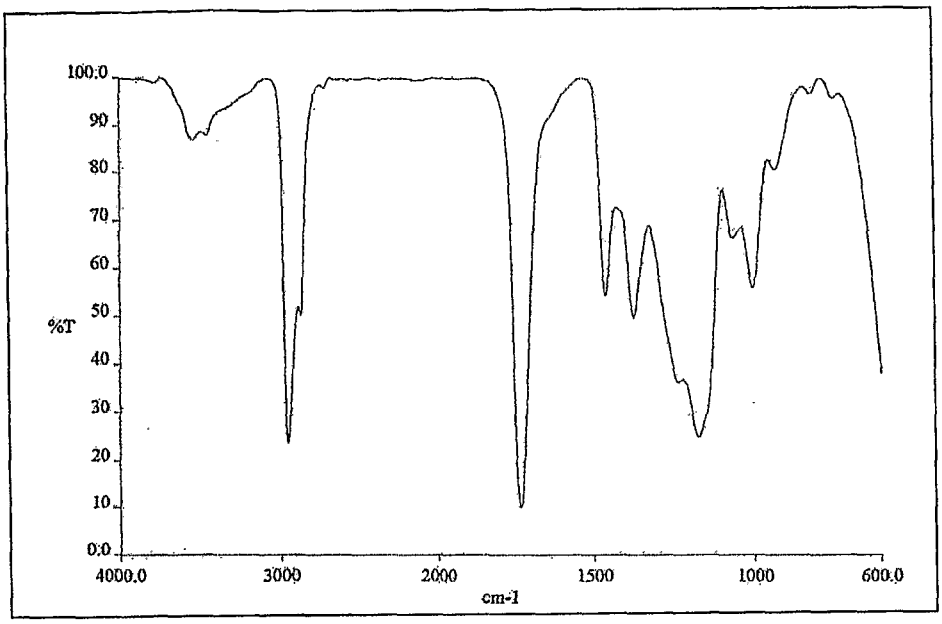


Figure 3: Infrared spectrum of the adipate ester.

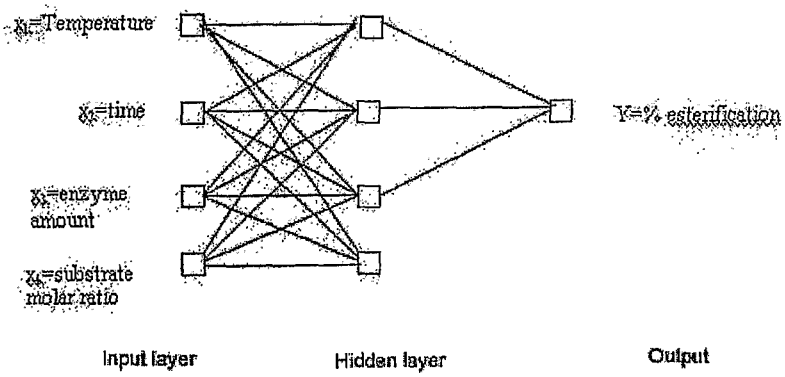


Figure 4: Schematic diagram of artificial neural network (ANN)

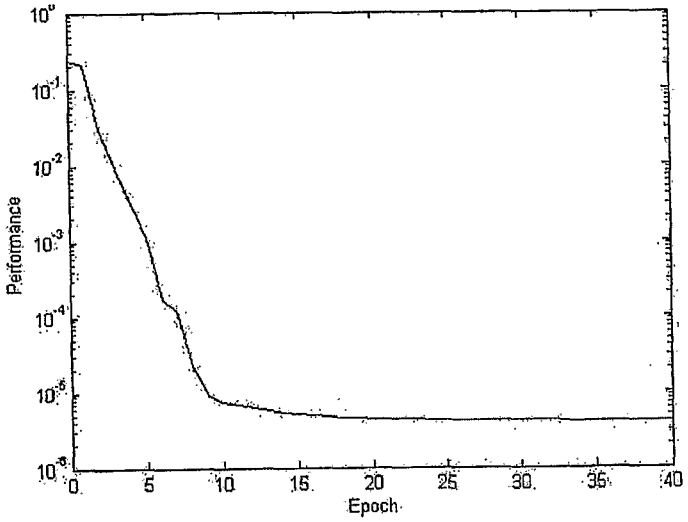


Figure 5: Mean squared error vs. epoch (cycle) during the training process

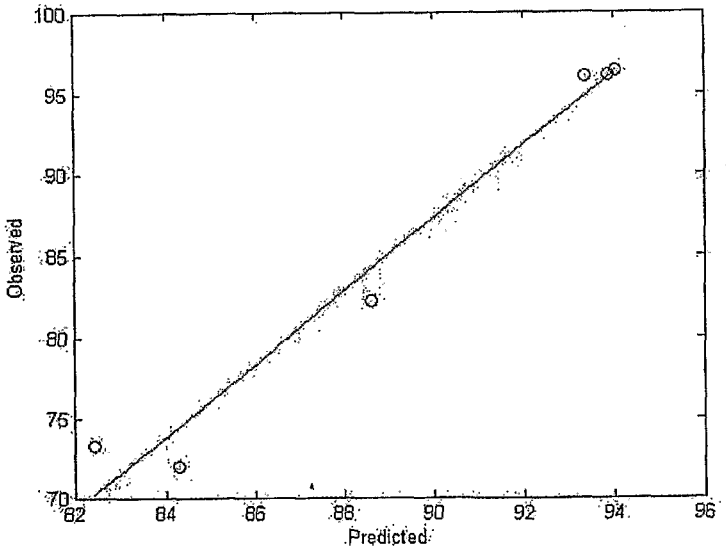


Figure 6: ANN correlation between the observed and predicted adipte ester yield.

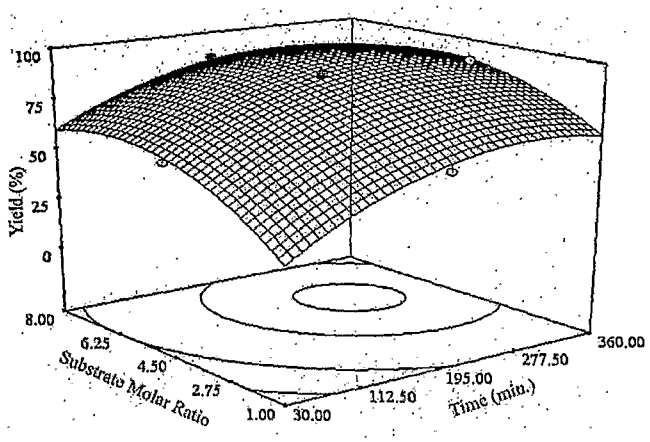


Figure 7: Response surface plot showing the effect of molar ratio, time and their interaction on the synthesis of adipate ester.

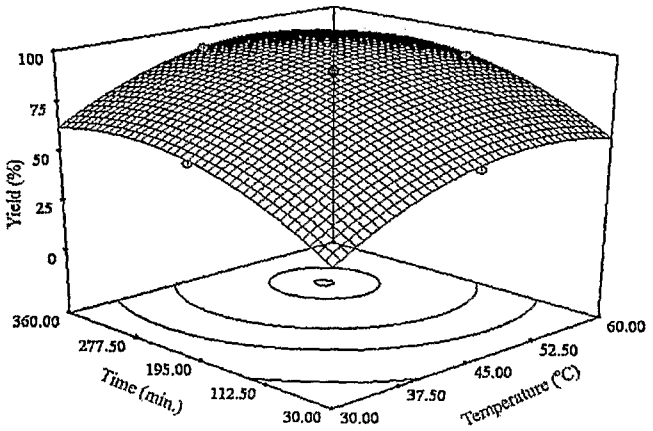


Figure 8: Response surface plot showing the effect of temperature, reaction time and their interaction on the synthesis of adipate ester.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/MY2008/000093

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

C12P 7/62 (2006.01) *C07C 69/44* (2006.01) *C12R 1/72* (2006.01)
C07C 67/08 (2006.01) *C12R 1/645* (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
STN: CA; EPOQUE: EPODOC, WPI (keyword search based on adipic acid; adipate ester; wax; fatty; enzyme; lipase; preparatory role).

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	EP 1775344 A2 (BEIJING UNIVERSITY OF CHEMICAL TECHNOLOGY) 18 April 2007 See Examples 18 and 19.	1-4, 6, 8 4, 7
X Y	RAHMAN, M. B. A. *et al.* "Enzymatic synthesis of methyl adipate ester using lipase from *Candida rugosa* immobilised on Mg, Zn and Ni of layered double hydroxides (LDHs)", Journal of Molecular Catalysis B: Enzymatic (2008), 50, 33-39. Available online 29 September 2007. See whole document.	8 4

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 October 2008	4 - NOV 2008
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. +61 2 6283 7999	Authorized officer **RACHEL KING** AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No : +61 2 6225 6127

INTERNATIONAL SEARCH REPORT

International application No.
PCT/MY2008/000093

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	BASRI, M. *et al.* "Comparison of estimation capabilities of response surface methodology (RSM) with artificial neural network (ANN) in lipase-catalyzed synthesis of palm-based wax ester", BMC Biotechnology (2007), 7(53), 14 pages. Available from: **http://www.biomedcentral.com/1472-6750/7/53** See whole document, particularly page 2, column 1, paragraph 4; page 2, column 1, paragraph 1.	7
A	SG 123626 (UNIVERSITI PUTRA MALAYSIA) 28 September 2007. See whole document.	1-4, 6-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/MY2008/000093

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member	
EP	1775344	CN	1948470
SG	123626	NONE	

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX

Materials

The chemicals used in this project are listed below with the names of supplier and were used as received without purification, unless otherwise stated.

Solvents	**Manufacturers**
Acetic acid	Merck, Germany
Acetone	J.T Baker, U.S.A
Chloroform	J.T Baker, U.S.A
Dichloromethane	Sigma-Aldrich, USA
Diethyl ether	Merck, Germany
Ethanol	J.T Baker, U.S.A
Hexane	J.T Baker, U.S.A
Heptane	Merck, Germany
Toluene	J.T Baker, U.S.A

Substrates	**Manufacturers**
Arachidyl alcohol	J.T Baker, U.S.A
Myristic acid, 99%	Merck, Germany

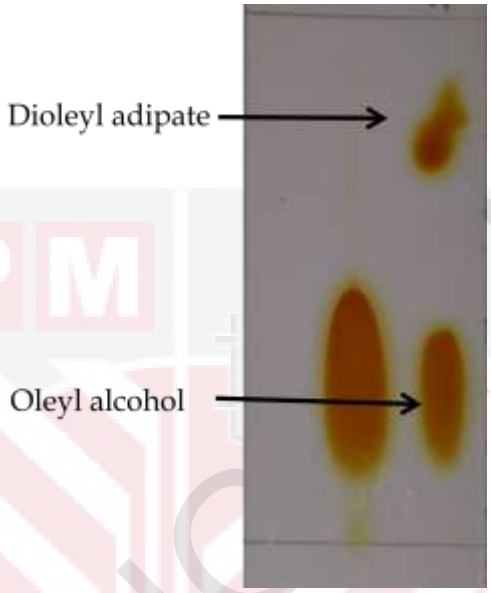
Oleic acid, 80%	Tokyo Kasei Co. Ltd., Japan
Palmityl alcohol	J.T Baker, U.S.A
Palmitic acid, 98%	Merck, Germany
Stearic acid, 95%	J.T Baker, U.S.A
1,5-Pentanediol	J.T Baker, U.S.A

Chemicals	**Manufacturers**
Benzophenone	Merck, Germany
Brij 30	Sigma Aldrich, USA
Brij 93	Sigma Aldrich, USA
Coomassie Brilliant Blue G-250	Fluka, Japan
Darocur® 1173	Ciba, Switzerland
Ebecryl 600 (EB600)	UCB Chemicals, Belgium
Hydrogen Peroxide, 30%	Mallinckrodt Baker, Mexico
Irgacure 500	Ciba, Switzerland
N-methyldiethanolamine	Sigma Aldrich, U.S.A
Pentaerythritol acrylate	UCB Chemicals, Belgium
Phenolphthalein	Sigma-Aldrich, USA
Phosphoric acid	J.T Baker, U.S.A

ρ-anisaldehyde	Merck, Germany
Sodium hydroxides	Mallinckrodt Baker, Mexico
Span 20	Fluka, Germany
Span 40	Merck, Germany
Triethylamine	Sigma Aldrich, U.S.A
Tween 20	Merck, Germany
Tween 40	Merck, Germany
Tween 60	Merck, Germany
Tween 80	Merck, Germany
Tween 85	Merck, Germany

Thin layer chromatogram of; (a) Dioleyl adipate. Developing Solvent:Chloroform: Hexane (8:2 v/v). R_f = 0.85. (b) Dilauryl adipate Developing Solvent: Chloroform: Dichloromethane (95:5 v/v) R_f = 0.57.

(a)



(b)

Thin layer chromatogram of; (a) Epoxidized oleate. Developing Solvent: Chloroform: Hexane: Acetic acid (8:2:0.1 v/v), R_f = 0.6; (b) Epoxidized linoleate. Developing Solvent: Chloroform: Hexane: Acetic acid (5:5:0.1 v/v) R_f = 0.85). (c) Epoxidized ricinoleate. Developing Solvent: Chloroform: Hexane: Acetic acid (5:5:0.1 v/v) $R_{f=}$ 0.7).

(a) **(b)** **(c)**

BIODATA OF STUDENT

Noraini Abd Ghani was born on the 2nd February 1982 and raised in Mersing, Johor. She had her primary education at Sekolah Kebangsaan Mersing Kanan, Mersing and continued her secondary education at Sekolah Menengah Kebangsaan Mersing, Johor. After completing her Penilaian Menengah Rendah in 1997 with 9A's, she was offered to further her study at Maktab Rendah Sains MARA, Jasin. In this boarding school, she completed her Sijil Pelajaran Malaysia in 1999 and she then pursued her pre –university education at Kolej Matrikulasi Kulim, Kedah. In 2002, she embarked on Bachelor Science majoring in Petroleum Chemistry at Universiti Putra Malaysia (UPM) and graduated in the year 2005 with second class upper.

Thereafter, she enrolled in the Master of Science programme at Faculty of Science, UPM where she was awarded a scholarship of Graduate Research Fund. During her third semester, she was offered to do conversion of her Master degree to Doctor of Philosophy in the same project. Later, she was embarked to do part of her research in Greenchem at Kemicentrum, Department of Biotechnology, Lund University, Sweden. She also has good opportunity in working with Akzo Nobel Industrial Coatings, Malmo, Sweden and Malaysia Nuclear Agency.

During her stay in UPM, she gained experiences as a part time laboratory instructor and research assistant at Department of Chemistry, Faculty of Science. She also attended several national and international conferences and exhibitions.

LIST OF PUBLICATIONS

Journals (Published/ Submitted)

1. Mohd Basyaruddin Abdul Rahman, **Noraini Abdul Ghani**, Nik Ghazali Nik Salleh, Mahiran Basri, Raja Noor Zaliha Raja Abdul Rahman and Abu Bakar Salleh. "Development of Coating Materials from Liquid Wax Esters for Wood Top-Based Coating" *Journal of Coatings Technology and Research* Volume 8, Issue 2 (2010), Page 229-236.
2. Cecilia Orellana Akerman, Yasser Gaber, **Noraini Abd Ghani**, Merja Lämsä and Rajni Hatti-Kaul. "Clean synthesis of biolubricants for low temperature applications using heterogenous catalysts." *Journal of Molecular Catalysis B: Enzymatic* Volume 72, Issues 3-4 (2011), Page 263-269.

Patent

1) Mohd Basyaruddin Abdul Rahman, **Noraini Abdul Ghani**, Naz Chaibakhsh Mahiran Basri, Raja Noor Zaliha Raja Abdul Rahman and Abu Bakar Salleh. "
   Invention : A Method for Producing Adipate Ester
   International Patent Application No. PCT/MY2008/000093 (3rd September 2008)
   Publication No. : WO/2009/066975 (28th May 2009)
   Malaysian Patent Application No P1 20072081 (23rd November 2007)

2) Mohd Basyaruddin Abdul Rahman, **Noraini Abdul Ghani**, Mahiran Basri, Raja Noor Zaliha Raja Abdul Rahman and Abu Bakar Salleh.
   Invention : Formulation for Coating Material
   United States Patent Application No. 12/515,373

International Patent Application No. PCT/MY2008/000094 (3rd September 2008)

Publication No. : WO/2009/066976 (28th May 2009)

Malaysian Patent Application No P1 20072080 (23rd November 2007)

Conferences and Exhibitions

1) Mohd Basyaruddin Abdul Rahman, **Noraini Abdul Ghani**, Naz Chaibakhsh, Mahiran Basri, Raja Noor Zaliha Raja Abdul Rahman and Abu Bakar Salleh. "Sustainable and Solventless Surface Coatings". Hari Harta Intelek Negara 2009 (HHIN09) Malaysian, 23-27 April 2009, Kuala Lumpur, Malaysia (*winner of Special Award*)
2) **Noraini Abdul Ghani**, Mohd Basyaruddin Abdul Rahman, Mahiran Basri, Raja Noor Zaliha Raja Abdul Rahman and Abu Bakar Salleh (2008). "Environmentally Benign Organic Production of Palm-based Epoxides", 19th *Annual National Symposium on Analytical Chemistry*, 25-27th November, Kota Kinabalu, Sabah.
3) Mohd Basyaruddin Abdul Rahman, **Noraini Abd Ghani**, Naz Chaibakhsh Langroodi, Mahiran Basri, Raja Noor Zaliha Raja Abdul Rahman, Abu Bakar Salleh, Paridah Md. Tahir and Nik Ghazali Nik Salleh (2008). Sustainable and Solventless Surface Coatings", *Innovation Nuclear*, 16-18th July, Agency Nuclear Malaysia. (*winner of Silver Award*)
4) Mohd Basyaruddin Abdul Rahman, **Noraini Abd Ghani**, Mahiran Basri, Raja Noor Zaliha Raja Abdul Rahman, Abu Bakar Salleh, Paridah Md. Tahir and Nik Ghazali Nik Salleh (2008). "MBiocoatings : Nanoformulation Surface Coating", *Invention and New Product Exposition Expo* (INPEX 2008), 11-14th June, Pittsburgh, USA.
5) Mohd Basyaruddin Abdul Rahman, **Noraini Abd Ghani**, Naz Chaibakhsh Langroodi, Mahiran Basri, Raja Noor Zaliha Raja Abdul Rahman and Abu Bakar Salleh (2008). "Liquid Wax Esters", *Invention and New Product Exposition Expo* (INPEX 2008), 11-14th June, Pittsburgh, USA.

6) **Mohd** Basyaruddin Abdul Rahman, **Noraini Abd Ghani**, Mahiran Basri, Raja Noor Zaliha Raja Abdul Rahman, Abu Bakar Salleh and Nik Ghazali Nik Salleh (2008). "Adipate Ester Formulation for Radiation Curing of Surface Coatings" *4th International Conference on X-rays and Related Techniques in Research and Industry (ICXRI 2008) "Strengthening Networking in X-Ray Technology"* 2-6 June, Kota Kinabalu, Sabah.

7) Mohd Basyaruddin Abdul Rahman, **Noraini Abdul Ghani**, Naz Chaibakhsh, Mahiran Basri, Raja Noor Zaliha Raja Abdul Rahman and Abu Bakar Salleh. "Sustainable Production of High Value Added Adipate Esters for Surface Coatings". Malaysian Technology Expo (MTE) 2008, 21-23 Februari 2008, Kuala Lumpur, Malaysia (*winner of Gold Medal*)

8) Mohd Basyaruddin Abdul Rahman, **Noraini Abd Ghani**, Mahiran Basri, Raja Noor Zaliha Raja Abdul Rahman, Abu Bakar Salleh, Paridah Md. Tahir and Nik Ghazali Nik Salleh (2007). "MBiocoatings™: Green Route Wax Ester Formulation for Surface Coatings", *Exhibition of Invention, Research & Innovation* (PRPI 2007), 27-29th November, UPM. (*winner of Silver Medal*)

9) **Noraini Abdul Ghani**, Mohd Basyaruddin Abdul Rahman, Muhammad Aliff Mohamad Latiff, Mahiran Basri, Raja Noor Zaliha Abdul Rahman and Abu Bakar Salleh, "Synthesis of Petro-based Di-isobutyl Adipate by Immobilized Lipase", 12th Asian Chemical Congress, 23-25th August 2007, Kuala Lumpur, Malaysia.

10) Mohd Basyaruddin Abdul Rahman, **Noraini Abd Ghani**, Ng Shie Ling, Mahiran Basri, Raja Noor Zaliha Raja Abdul Rahman and Abu Bakar Salleh (2007). "Green Route Production of Petro-based Adipate Esters" *Selangor Young Scientist Competition*, 12-15th July, Shah Alam, Selangor. (*winner of Overall Excellent Young Scientist Award and Champion for Product Innovation*)

11) Mohd Basyaruddin Abdul Rahman, **Noraini Abd Ghani**, Ng Shie Ling, Mahiran Basri, Raja Noor Zaliha Raja Abdul Rahman and Abu Bakar Salleh (2007). "Green Route Production of Petro-based Adipate Esters" *Research & Development Exposition – PECIPTA 2007*, 22-24th August, KL Convention Center.

12) Mohd Basyaruddin Abdul Rahman, **Noraini Abd Ghani**, Ng Shie Ling, Mahiran Basri, Raja Noor Zaliha Raja Abdul Rahman and Abu Bakar Salleh (2006). "Green Route Production of Petro-based Adipate Esters" *Exhibition of Invention, Research & Innovation* (PRPI 2006), 22-24th August, UPM. (*winner of Gold Medal*)