UNIVERSITI PUTRA MALAYSIA

IMPROVING PURITY OF BIO-BASED CROTONIC ACID

NUR FALIA SHAZANA MANJA BINTI FARID

FBSB 2015 11

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

IMPROVING PURITY OF BIO-BASED CROTONIC ACID

By

NUR FALIA SHAZANA MANJA BINTI FARID

June 2015

Chairman : Hidayah Ariffin, PhD
Faculty : Biotechnology and Biomolecular Sciences

Crotonic acid is an unsaturated carboxylic acid derived from petroleum resource which is currently used as components of hair styling products, insecticides, softening agent for synthetic rubber and plasticizer. At present, commercial crotonic acid is chemically synthesized from non-renewable resource through multi-step chemical synthesis. Recently, bio-based crotonic acid production has been introduced through pyrolysis of bacterial polyhydroxybutyrate (P(3HB)) inclusions, however the purity of the crotonic acid produced was low (54%). Therefore, this study was done aimed at improving the purity of bio-based crotonic acid. In this study, P(3HB) was produced by *Cupriavidus necator* KCTC 2649 utilizing oil palm frond (OPF) juice. P(3HB) inclusion produced had the purity of 75%. Effect of mild alkali pretreatment on P(3HB) purity and subsequently crotonic acid purity was tested by using 0.05M NaOH. It was found that crotonic acid produced from NaOH-treated P(3HB) had purity of 92 %. Results from this study showed that NaOH treatment not only caused the improvement in P(3HB) purity which consequently caused the increment in crotonic acid purity, but it also caused the molar mass of the P(3HB) to reduce to form lower molar mass P(3HB) with crotonyl chain-end. This condition accelerated β-chain scission of P(3HB) into crotonic acid. Additionally, NaOH treatment caused the presence of Na metal cation which initiated α-deprotonation of P(3HB), followed by the formation of unsaturated crotonic acid. It was believed that the purity of the crotonic acid produced can be improved by introducing metal compounds during pyrolysis of NaOH-treated P(3HB) in order to selectively degrade the P(3HB) into crotonic acid. Results revealed that the type of metal cation used caused a marked different in crotonic acid formation, whereby $MgCl_2$ gave the highest crotonic acid purity at 92 %, followed by NaCl and $CaCl_2$ at 90 and 88 %, respectively. This observation was contributed by ion size of the cation; the smaller the size of the cation, the higher the crotonic acid produced. On the other hand, the effect of anion was not pronounced as all the anions of Mg compounds used *i.e.* Cl^-, OH^- and O^{2-} gave almost similar crotonic acid purity at 98-99%. Overall, it can be concluded that the purity of bio-based crotonic acid was tremendously improved with mild alkaline pre-treatment and addition of alkaline earth compounds. The results from this study contribute to the novel and renewable production of high purity bio-based crotonic acid.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

MENINGKATKAN KETULENAN ASID KROTONIK BERASASKAN BIO

Oleh

NUR FALIA SHAZANA MANJA BINTI FARID

Jun 2015

Pengerusi : Hidayah Ariffin, PhD
Fakulti : Bioteknologi dan Sains Biomolekul

Asid krotonik adalah asid karboksilik tak tepu yang diperolehi daripada sumber petroleum yang pada masa kini digunakan sebagai komponen produk penggayaan rambut, racun serangga, agen pelembut untuk getah sintetik dan bahan peliat plastik. Pada masa kini, asid krotonik komersial disintesis daripada sumber yang tidak boleh diperbaharui melalui sintesis kimia pelbagai langkah. Baru-baru ini, pengeluaran asid krotonik berasaskan bio telah diperkenalkan melalui pirolisis daripada polihidroksibutirat (P(3HB)) dalam bakteria, walaubagaimanapun ketulenan asid krotonik yang dihasilkan adalah rendah (54 %). Oleh itu, kajian ini dilakukan bertujuan untuk meningkatkan ketulenan asid krotonik yang berasaskan bio. Dalam kajian ini, P(3HB) telah dihasilkan oleh *Cupriavidus necator* KCTC 2649 yang menggunakan jus pelepah kelapa sawit (OPF). P(3HB) dalam bakteria yang dihasilkan mempunyai ketulenan 75 %. Kesan alkali sederhana sebagai pra-rawatan kepada ketulenan P(3HB) dan seterusnya ketulenan asid krotonik telah diuji dengan menggunakan 0.05M NaOH. Didapati bahawa asid krotonik yang dihasilkan dari P(3HB) yang dirawat dengan NaOH (P(3HB)-NaOH) mempunyai ketulenan 92 %. NaOH bukan sahaja menyebabkan peningkatan dalam ketulenan P(3HB) yang seterusnya menyebabkan peningkatan dalam ketulenan asid krotonik, tetapi ia juga menyebabkan jisim molar P(3HB) berkurang untuk membentuk P(3HB) yang mempunyai jisim molar yang lebih rendah dengan rantaian-akhir krotonil. Keadaan ini mempercepatkan pemecahan rantaian-β P(3HB) kepada asid krotonik. Selain itu, rawatan NaOH menyebabkan kehadiran logam kation Na yang memulakan *α-deprotonation* P(3HB), diikuti dengan pembentukan asid krotonik tak tepu. Adalah dipercayai bahawa ketulenan asid krotonik yang dihasilkan dapat ditingkatkan dengan memperkenalkan sebatian logam semasa pirolisis P(3HB)-NaOH yang dirawat untuk menguraikan P(3HB) kepada asid krotonik secara terpilih. Keputusan menunjukkan bahawa jenis kation logam yang digunakan menyebabkan perbezaan ketara dalam pembentukan asid krotonik, di mana $MgCl_2$ memberi ketulenan asid krotonik tertinggi pada 92 % , diikuti oleh NaCl dan $CaCl_2$, masing-masing pada 90 dan 88 %. Pemerhatian ini adalah disebabkan oleh saiz kation; di mana semakin kecil saiz kation, semakin tinggi asid krotonik dihasilkan. Sebaliknya, kesan anion tidak ketara kerana semua anion sebatian Mg yang digunakan iaitu Cl^- , OH^- dan O^{2-} memberikan ketulenan asid krotonik yang hampir sama pada 98-99 %. Secara keseluruhan, dapat disimpulkan bahawa ketulenan asid krotonik berasaskan bio meningkat secara ketara dengan menggunakan pra-rawatan alkali sederhana dan penambahan sebatian alkali bumi. Hasil daripada kajian ini menyumbang kepada

pengeluaran asid krotonik berasaskan bio yang berketulenan tinggi secara asli dan boleh diperbaharui.

ACKNOWLEDGEMENTS

In The Name Of Allah, the Most Gracious, the Most Merciful

Alhamdulillah. Thanks to Allah SWT, for with His willing I am able to complete my master research. I am very grateful since I have been given the strength and patience to complete this research successfully and thesis as well.

I would like to express my deep and sincere gratitude to my supervisor, Dr. Hidayah Ariffin, for her encouragement, support, guidance, motivation and many valuable discussions from the initial to the final stage of my research. Her guidance helped me in all the time of research and writing of this thesis. I also would like to express my deepest gratitude to my co-supervisors Prof. Dr. Mohd Ali Hassan and Dr. Mior Ahmad Khushairi Bin Mohd Zahari for detailed and constructive comments, guidance, suggestion and unconditional support that greatly eased my progress throughout this study.

My condensed thanks go to Nur Sharmila Sharip, Mohd Rahimi Zakaria, Noor Farisha and Che Mohd Hakiman for their kind helps and supports with some of the laboratory works during my study. I also wish to extend my sincere gratitude to all my friends, FUN members, and others who helped and gave me support, guidance, helpful suggestions as well as proof-read my paper and thesis.

I also would like to express my greatest gratitude to my father, Farid Bin Mohd Noor and my mother, Rosmawati Abd Rahman who always be there when I need support and understand me in whatever condition. My deepest thanks and appreciation also goes to my others family members, and my husband, Ahmad Anif Bin Ramli for their love, prayer, and moral support for me. They prevented me from feeling lost and give up during my study as well as helped me by giving me unconditional supports.

This list is far from exhaustive, I pray for forgiveness from those I did not mention by name and include then in my heart-felt gratitude.

I certify that Thesis Examination Committee has met on to conduct the final examination of **Nur Falia Shazana Manja Binti Farid** on her **Master of Science** thesis entitled **"Improved purity of bio-based crotonic acid"** in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The committee recommends that the student be awarded the Master of Science.

Members of the Thesis Examination Committee were as follows:

Mohd Shukuri Mohamad Ali, PhD
Senior Lecturer
Faculty of Biotechology and Biomolecular Sciences
Universiti Putra Malaysia
(Chairman)

Umi Kalsom Md Shah, PhD
Associate Professor
Faculty of Biotechology and Biomolecular Sciences
Universiti Putra Malaysia
(Internal Examiner)

Amirul Al-Ashraf Abdullah, PhD
Associate Professor
School of BIologival Sciences
Universiti Sains Malaysian
Malaysia
(External Examiner)

SEOW HENG FONG, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members for the Supervisory Committee were as follows:

Hidayah Ariffin, PhD
Senior Lecturer
Faculty of Biotechology and Biomolecular Sciences
Universiti Putra Malaysia
(Chairman)

Mohd Ali Hassan, PhD
Professor
Faculty of Biotechology and Biomolecular Sciences
Universiti Putra Malaysia
(Member)

Mior Ahmad Khushairi Mohd Zahari, PhD
Senior Lecturer
Faculty of Chemical and Natural Resources Engineering
Universiti Malaysia Pahang
(Member)

BUJANG BIN KIM HUAT, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

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(GS33597)

Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
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Signature: _____
Name of Chairman of Supervisory Committee: Hidayah Ariffin, PhD

Signature: _____
Name of Chairman of Supervisory Committee: Mohd Ali Hassan, PhD

Signature: _____
Name of Chairman of Supervisory Committee: Mior Ahmad Khushairi Bin Mohd Zahari, PhD

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LIST OF ABBREVIATIONS

ΔH	Melting enthalpy of the sample
^{1}H-NMR	Proton nuclear magnetic resonance
2HB	2-hydroxybutyrate
3HB	3-hydroxybutyrate
3HHx	3-hydroxyhexanoate
3HV	3-hydroxyvalerate
3HV	3-hydroxyvalerate
4HB	4-hydroxybutyrate
4HV	4-hydroxyvalerate
AAm	Acrylamide
AAS	Atomic absorption spectrophotometer
AMPS	Acrylamido-2-methyl-1-propanesulfonic acid
CA	Crotonic acid
$Ca(Cl)_2$	Calcium Chloride
$CDCl_3$	Chloroform –d
CO_2	Carbon dioxide
CoA	Coenzyme A
$CuCl_2$	Copper chloride
DNS	3,5-Dinitrosalicylic acid
DSC	Differential scanning calorimetry
ESI-MS	Electrospray ionization-MS
FAB-MS	Fast atom bombardment mass spectrometry
FID	Flame ionization detector
FTIR	Fourier transform infrared spectrometry
GC-MS	Gas chromatography mass spectrometry
GPC	Gel permeation chromatography
GTO	Glass tube oven
H_0	100% crystalline P(3HB)
H_2O	Water
MCL	Medium-chain-length
$Mg(Cl)_2$	Magnesium Chloride
$Mg(OH)_2$	Magnesium Hydroxide
MgO	Magnesium Oxide
MS	Mass spectrometry
MSM	Mineral salt medium
MTBE	Methyl tert-butyl ether
NaCl	Sodium Chloride
NMR	Nuclear magnetic resonance
NPCM	Non-PHA cellular mass
PHA	Polyhydroxyalkanoate
P(3HB)	Poly(3-hydroxybutyrate)
P(3HB)HHx	Polyhydroxybutyrate-co-hydroxyhexanoate
P(3HB)V	Poly-(3-hydroxybutyrate-co-3-hydroxyvalerate)
PP	Polypropylene

Py-GC	Pyrolysis-gas chromatography
Py-MS	Pyrolysis-mass spectrometry
SCL	Short-chain-length
SDS	Sodium dodecyl suphate
TEM	Transmission electron microscopy
TG	Thermo gravimetry
TGA	Thermo gravimetry analyzer
TIC	Total ion current
T_m	Melting temperature
TMS	Tetramethylsilane
UV	Ultraviolet
X_c	Degree of crystallinity

CHAPTER 1

INTRODUCTION

1.1 Overview of research

Many countries are moving towards a more sustainable bio-based economy derived from biomass compared to the current fossil-based economy (Ed *et al.*, 2012). Bio-based economy refers to the economy that uses biomass to produce products, chemicals, materials, biofuels and energy (Faaij *et al*., 2011). This movement is contributed by several factors, for example depletion of existing fossil raw materials, environmental concern and the consumer demand for environmental friendly products (Bechthold *et al*., 2008).

There are varieties of biomass feedstock such as sugars, vegetable oils, proteins and lignocellulosics which can be combined with numerous biochemical and thermochemical conversion technologies in order to provide wide range of products that can be used in many applications. Bio-based chemicals targeted markets include the polymer, lubricant, solvent, adhesive, herbicide, and pharmaceutical markets (Carole *et al*., 2004).

Crotonic acid and its derivatives is one of the promising chemicals in chemical industry due to their roles in many applications. Currently, crotonic acid is produced by multiple-step petroleum cracking process which involved the formation of by-products (Weissermel& Arpe, 2003). This method can be considered as non-environmental friendly since it uses non-renewable resource and produces polluted waste as by-product. Several approaches have been taken to produce crotonic acid from renewable resources (Koch & Meurer, 2012; Mamat *et al*., 2014; Schmid & Mauch, 2008; Van Walsem *et al*., 2012). Mamat and the colleague (2014) have recently proposed a bio-based crotonic acid production from renewable resource by manipulating the thermal degradation pathway of bacterial poly(3-hydroxybutyrate), P(3HB) inclusion. The proposed method is not only advantageous compared to petroleum-based crotonic acid in term of renewability, but also in terms of reduced number of processing step and higher yield by 30%. Due to its simplicity, crotonic acid from thermally degraded P(3HB) possesses great potential for industrial production. Nevertheless, despite of its higher yield compared to petroleum route, the crotonic acid purity obtained from direct pyrolysis of P(3HB) bacterial inclusion is low due to the presence of P(3HB) oligomers and other impurities from bacterial cell. It is therefore among the aims of this research was to improve the production of bio-based crotonic acid by increasing the purity of the bio-based crotonic acid.

The usual P(3HB) recovery and purification method to obtain high purity P(3HB) is by using halogenated organic solvent such as chloroform. It produced P(3HB) with very high purity (~99%), however this method is non-environmental friendly, costly, hazardous and having difficulty in the disposal of the wastewater (Chotani *et al*., 2012; McChalicher *et al*., 2010). Low cost, strong alkaline such NaOH and KOH have been

reported to be the ideal solvent for purification of P(3HB) since it efficiently digests non-polymeric cellular material (NPCM) (Choi & Lee, 1999). Mohammadi (2011) has reported that the use of low concentration NaOH can assist in the extraction of polyhydroxyalkanoates (PHA) to give PHA with 96% purity and recovery yield.

The conversion of P(3HB) into crotonic acid can be improved by using alkali earth compounds as catalyst (Ariffin *et al*., 2010b; Kawalec *et al*., 2007; Kim *et al*., 2006). Ariffin *et al*. (2010b) reported that selective transformation of P(3HB) into *trans*-crotonic acid can be obtained when $Mg(OH)_2$ was used as catalyst during pyrolysis. Additionally, oligomers composition was drastically reduced caused the high purity of crotonic acid in the pyrolyzate sample.

1.2 Problem statement

Mamat *et al*., (2014) suggested that direct pyrolysis of P(3HB) bacterial inclusions can be used to produce crotonic acid from renewable resources. The process involved fermentation of P(3HB) producing bacteria followed by thermal degradation of P(3HB) inclusions (P(3HB) biomass) at optimized temperature to obtain the crotonic acid. The crotonic acid produced had purity of 54% with 63% recovery yield. Purification step will be needed in order to produce pure crotonic acid. It was postulated that the low crotonic acid purity obtained from direct pyrolysis of P(3HB) bacterial inclusion was due to the volatilization of the other bacterial cell composition (non-polymeric cellular material, NPCM) during the pyrolysis.

Additionally, incomplete degradation of P(3HB) caused the production of oligomers which affected the purity of crotonic acid in pyrolyzates. It was hypothesized that these two issues can be solved by introducing P(3HB) pretreatment prior to pyrolysis followed by the use of catalyst during pyrolysis. Mohammadi *et al*. (2012) reported that treatment of P(3HB) with 0.05M NaOH was efficient to saponify lipid layer in the cell wall outer membrane and improve cell permeability that caused high purity of P(3HB) after the treatment. On the other hand, the use of $Mg(OH)_2$ as catalyst during pyrolysis caused almost complete conversion (> 98%) of P(3HB) into crotonic acid (Ariffin *et al*., 2010b). It is therefore this research was aimed at studying the combined effect of P(3HB) pretreatment with mild NaOH prior to pyrolysis and the addition of catalyst during pyrolysis on the formation and purity of crotonic acid.

1.3 Objectives

The objectives of this research are:

- To determine the effect of P(3HB) pretreatment prior to pyrolysis on the recovery yield and purity of crotonic acid.
- To evaluate the effect of alkali earth compounds as catalyst on the production of crotonic acid.

1.4 Thesis overview

Chapter 1 of this thesis introduces the problem statements and objectives of this research. This is followed by Chapter 2 where a summary of other researchers' findings are being discussed. Among the topics discussed were introduction of PHA includes its diversity, production, recovery methods and applications. Besides, dehydrated monomer of P(3HB), *i.e.* crotonic acid was discussed in detail. The review also includes thermal degradation of P(3HB), pyrolysis of P(3HB) and catalytic pyrolysis of P(3HB).

Chapter 3 covers general materials and methods of the research. This includes bacterial strain, *i.e. Cupriavidus necator* KCTC 2649, biosynthesis of P(3HB) and general analytical procedures.

Effect of P(3HB) pretreatments on the recovery yield and purity of crotonic acid is discussed in Chapter 4. Two types of pretreatment methods: chloroform extraction and NaOH treatment were studied and compared with untreated P(3HB) biomass. Untreated and treated P(3HB) were subjected to pyrolysis in the glass tube oven, and the pyrolyzates obtained was collected and analyzed by GC-MS and ^{1}H-NMR. Besides, other analysis such as TEM, AAS, GPC and FTIR analysis was carried out to support the data of GC-MS analysis.

Chapter 5 explores the effect of alkali earth compounds as catalyst for the production of crotonic acid. In this chapter, the effect of different metals and anions were studied. The P(3HB) recovered by NaOH was added with 5% of different catalyst to find the best catalyst in order to get high purity of crotonic acid.

In Chapter 6, the summary and conclusion of this study were presented. Recommendations for future work were also suggested.

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