

UNIVERSITI PUTRA MALAYSIA

BIOHYDROGEN PRODUCTION FROM SAGO HAMPAS BY Clostridium butyricum A1

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FBSB 2014 22



BIOHYDROGEN PRODUCTION FROM SAGO HAMPAS BY Clostridium butyricum A1

By

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Thesis Submitted to the School of Graduates Studies, Universiti Putra Malaysia, in Fulfilment of the Requirement for the Degree of Master of Science

June 2014

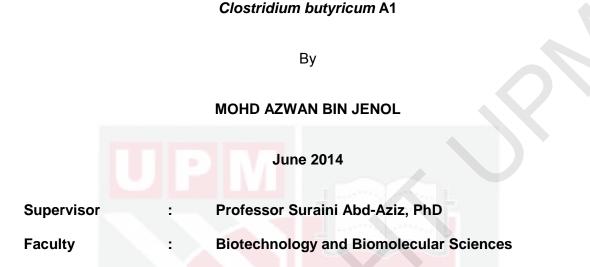
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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

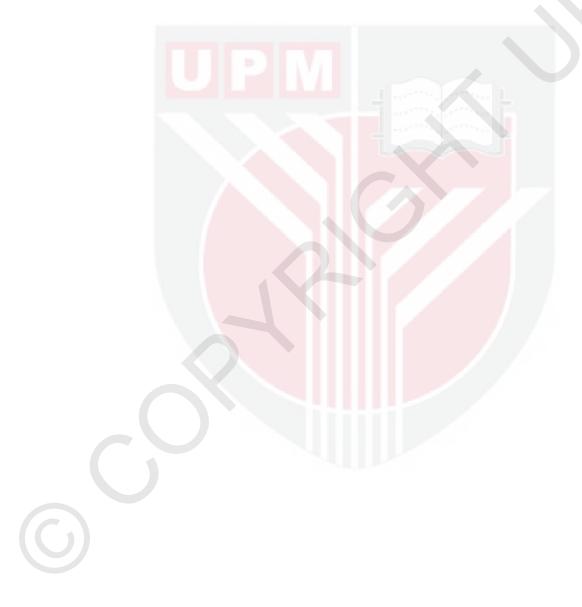
BIOHYDROGEN PRODUCTION FROM SAGO HAMPAS BY



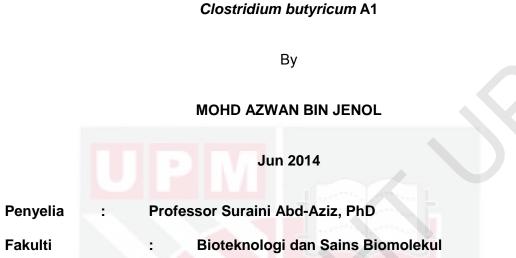
The hydrogen has been applied in fuel cell vehicle and expected to shift toward the technologies that produce no net greenhouse gas effects. Biohydrogen production from biomass is now attracting many researchers in developing a renewable, clean and environmental friendly biofuel. The availability of abundant biomass from various sources could possibly be an advantage for the production of biohydrogen as a competitive energy carrier in the future. There are vast choices of possible types of biomass that can be subjected as the carbon source for the production of biohydrogen including starch based and lignocellulosic biomass. Sago industry is one of the possible source of biomass since the industry is producing large quantities of starch and lignocellulosic biomass. Statistically, a single sago starch processing mill has produced 7 ton/day of sago *hampas*. Thus, this study aimed to produce biohydrogen from sago biomass by locally isolated biohydrogen producer and to optimize the production of biohydrogen using statistical approach.

The locally isolated biohydrogen producer *Clostridium butyricum* A1 was successfully isolated from landfill soil. This strain produced a biohydrogen yield of 1.90 mol H₂/mol glucose with productivity of 170 mL/L/h using pure glucose as substrate. The highest cumulative biohydrogen collected after 24 h of fermentation time was 2468 mL/L-medium. Biohydrogen fermentation using sago *hampas* hydrolysate generate higher biohydrogen yield (2.65 mol H₂/mol glucose) compared to sago pith residue (SPR) hydrolysate at 2.23 mol H₂/mol glucose. A higher biohydrogen productivity of 1757 mL/L/h was obtained when using sago *hampas* hydrolysate much higher when compared to pure glucose at 170 mL/L/h. In this study, the new isolate *C. butyricum* A1 together with the use of sago biomass as the substrate is a promising technology for future biohydrogen production. Optimization of biohydrogen production from sago *hampas* hydrolysate by *C. butyricum* A1 was conducted using four variables including temperature, sugar concentration, initial pH and inoculum size. This study has applied central composite design (CCD) and artificial neural network (ANN) as the optimization

step. As a result, three out of four variables have given significant effects on the production of biohydrogen from sago *hampas* hydrolysate; which are temperature, sugar concentration and pH. Using ANN, pH was found to be the most significant variable with the relative importance of 73.6%. The optimum conditions given by ANN with respect to optimized biohydrogen yield of 2.92 mol of H₂/mol of glucose are 39°C, pH 8, initial glucose concentration at 13 g/L and 13% (v/v) inoculum size. As conclusions, biohydrogen production from sago *hampas* by *C. butyricum* A1 has successfully conducted and optimized.



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

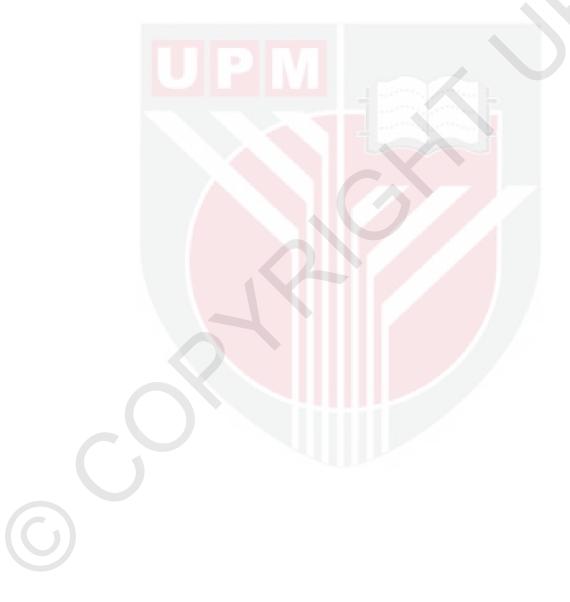


PENGHASILAN BIOHIDROGEN DARIPADA HAMPAS SAGU OLEH

Hidrogen telah diaplikasikan dalam kenderaan sel fuel dan dijangka akan menggerakkan teknologi yang tidak menghasilkan kesan gas rumah hijau. Penghasilan biohidrogen daripada biomas telah menarik minat ramai penyelidik dalam melestarikan penghasilan bahan api biologi yang boleh diperbaharui, bersih dan mesra alam. Ketersediaan biomas yang banyak daripada pelbagai sumber menjadi kelebihan pada penghasilan biohidrogen sebagai pembawa tenaga yang lebih berdaya saing pada masa hadapan. Pelbagai jenis biomas boleh dijadikan sumber karbon untuk penghasilan biohidrogen, termasuklah biomas berasaskan kanji dan lignoselulosa. Industri pemprosesan sagu adalah salah satu sumber biomas berpotensi kerana industri ini menghasilkan biomas berasaskan kanji dan lignoselulosa. Secara statistiknya, satu kilang pemprosesan sagu kanji telah menghasilkan sisa empulur sagu sebanyak 7 tan/hari. Tujuan kajian ini adalah untuk menghasilkan biohidrogen daripada biomas sagu oleh mikroganisma penghasil biohidrogen pencilan tempatan dan meningkatkan penghasilan biohidrogen menggunakan pendekatan statistik.

Bakteria pencilan tempatan penghasil biohidrogen, Clostridium butyricum A1 telah berjaya dipencilkan daripada tanah tapak pelupusan. Bakteria ini telah berjaya menghasilkan biohidrogen sebanyak 1.90 mol H₂/mol glukosa dan 170 mL/L/j produktiviti dengan menggunakan glukosa tulen sebagai substrat. Biohidrogen kumulatif tertinggi yang telah dicatatkan selepas 24 j fermentasi adalah 2468 mL/L-media. Fermentasi biohidrogen menggunakan hidrolisat hampas sagu telah menghasilkan biohidrogen yang lebih tinggi (2.65 mol H₂/mol glukosa) berbanding hidrolisat sisa empulur sagu (SES) (2.23 mol H₂/mol glukosa). Kadar penghasilan biohidrogen yang tinggi juga telah dicatatkan dengan menggunakan hidrolisat hampas sagu iaitu 1757 mL/L/j berbanding dengan menggunakan glukosa tulen dengan produktiviti 170 mL/L/j. Dalam kajian ini, C. butyricum A1 bersama dengan penggunaan biomas sagu sebagai substrat menjanjikan satu teknologi yang berpotensi untuk penghasilan biohidrogen di masa hadapan. Pengoptimuman penghasilan biohidrogen daripada hidrolisat hampas sagu oleh C.

butyricum A1 telah dijalankan dengan berasaskan 4 pembolehubah, termasuklah suhu, kepekatan gula, pH awal dan saiz inokula. Kajian ini telah menggunakan *central composite design* (CCD) dan *artificial neural network* (ANN) di dalam proses pengoptimuman. Daripada hasil kajian, tiga dari empat pembolehubah telah memberikan kesan yang signifikan pada penghasilan biohidrogen daripada hidrolisat hampas sagu; iaitu suhu, kepekatan gula dan pH. Berdasarkan analisis menggunakan ANN, pH merupakan pembolehubah yang memberikan kesan yang paling ketara dengan kepentingan relatif sebanyak 73.6%. Keadaan yang optimum telah diberikan oleh ANN untuk penghasilan 2.92 mol H₂/mol glukosa ialah 39°C, pH 8, 13 g/L kepekatan glukosa dan saiz inokula 13% (v/v). Kesimpulannya, penghasilan biohidrogen daripada sisa empulur sagu oleh *C. butyricum* A1 telah berjaya dijalankan dan dioptimumkan.



ACKNOWLEDGEMENTS

Alhamdulillah, by the blessing of Allah S.W.T., I manage to complete the thesis entitled "Biohydrogen production from sago *hampas* by *Clostridium butyricum* A1" for my Degree of Master of Science. In completing this project, I would like to express my deep and appreciation to everyone that have helped me. First of all, I would like to thank my main supervisor, Professor Dr. Suraini Abd-Aziz, who is willing to guide, critic and encourage me throughout this project. Without her, this project would not be complete, as presented here.

I would also like to present my appreciation to my supervisor's committee, Assoc. Prof. Dr. Madihah Md Salleh and Dr. Phang Lai Yee, who willing to advise and encourage me in order to finish up my Master of Degree project. Also, to Dr. Mohamad Faizal Ibrahim, who is willing to guide and give a lot of assistances, in helping me throughout my experimental works. They are willing to spend the time for me throughout the project and thesis writing progress.

I am also grateful to all Environmental Biotechnology (EB) group members, Universiti Putra Malaysia, for helping me in terms of advice and suggestion. Also, I would like to express my gratitude to Universiti Putra Malaysia and Malaysia Education Ministry (MOE) for supporting my funding in my three years study.

Last but not least, I would like to express my deepest appreciation to all my family members for their moral supports, especially my beloved mum, Fauziah bte Mustapa, and my sisters, Suliana bte Jenol and Noraisyah bte Jenol. Their endless love, support, and encouragement have made me a better person.

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

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TABLE OF CONTENTS

	Page
ABSTRACT	i
ABSTRAK	iii
ACKNOWLEDGEMENTS	V
APPROVAL	vi
DECLARATION	viii
LIST OF TABLES	xii
LIST OF FIGURES	xiii
LIST OF ABBREVIATIONS	xiv
CHAPTER	

1	INTRODUCTION	1
2	LITERATURE REVIEW 2.1 Introduction 2.2 Biomass 2.2.1 Starch based biomass 2.2.2 Lignocellulosic biomass	5 5 6 9
	2.3 Sago biomass in Malaysia 2.3.1 Sago waste	13 13
	 2.4 Overview of hydrogen 2.5 Hydrogen production 2.5.1 Steam reforming methane 2.5.2 Water hydrolysis 2.5.3 Fermentation process 	17 18 19 20 20
	2.6 Biohydrogen fermentation 2.6.1 Microorganisms 2.6.2 Substrates 2.6.3 Fermentation types	20 20 21 24
	 2.7 Factors affecting biohydrogen production 2.7.1 pH 2.7.2 Temperature 2.7.3 Substrate concentration 2.7.4 Inoculum size 2.7.5 Others 	27 27 27 28 28 29
	 2.8 Statistical optimization 2.8.1 Response surface methodology 2.8.2 Artificial neural network 2.8.3 Others 	29 29 31 32
3	 MATERIALS AND METHODS 3.1 General experimental design 3.2 Substrate preparation 3.3 Identification of biohydrogen producer 3.3.1 DNA extraction 3.3.2 PCR amplification, sequencing and phylogenetic analysis 	33 33 35 35 36 36

	3.4	Cellulase production	36
	3.5	Saccharification process	37
		3.5.1 Sago hampas	37
		3.5.2 Sago pith residue	38
	3.6	Biohydrogen production	38
		3.6.1 Inoculum preparation	38
		3.6.2 Medium preparation	38
		3.6.3 Fermentation process	39
	3.7	Optimization of biohydrogen production	39
		3.7.1 Central composite design	39
	<u> </u>	3.7.2 Artificial neural network	40
	3.8	Analytical procedures	41
		3.8.1 Determination of cellulose, hemicellulose and	14
		lignin content	41
		3.8.2 Determination of starch content 3.8.3 Cell concentration	43 43
		3.8.4 Amylase assay	43
		3.8.5 Cellulase activity assay	43
		3.8.6 Sugars determination	44
		3.8.7 Biohydrogen analysis	47
	3 9 T	The kinetic study	48
	0.0 1	The Kinetio otady	10
4	RES	ULTS AND DISCUSSION	49
	4.1	Chemical composition of sago biomass	49
	4.2		51
	4.3	Identification and phylogenetic analysis of biohydrogen	
		producer	53
	4.4	Biohydrogen production using different types of carbon	
		source	55
		4.4.1 Glucose	55
		4.4.2 Sago hampas hydrolysate	58
		4.4.3 Sago pith residue hydrolysate	59
		4.4.4 Comparison study	62
	4.5	Optimization of biohydrogen production using	05
		statistical analyses	65
		4.5.1 Central composite design approach 4.5.2 Artificial neural network approach	65 71
		4.5.2 Artificial neural network approach	71
5	CON	ICLUSION AND RECOMMENDATIONS	73
REFEREN			76
APPENDI			99
BIODATA			105
LIST OF F	UBL	ICATIONS	106

LIST OF TABLES

Table		Page
2.1	The physicochemical characteristics of starchy-based wastewater	15
2.2	Four basic sections in the steam reforming methane plant	19
2.3	Overview of biohydrogen production from starch based and lignocellulosic biomass	23
2.4	An overview of biohydrogen production via dark and photo fermentation	25
3.1	The coded values for each variable for CCD	39
4.1	An overview of chemical composition of biomass	50
4.2	The hydrolysis of several types of biomass	51
4.3	Biohydrogen production by <i>Clostridium butyricum</i> A1 and <i>Clostridium butyricum</i> EB6 using synthetic glucose, sago <i>hampas</i> hydrolysate and sago pith residue hydrolysate	60
4.4	Summary of biohydrogen production using different types of carbon source	63
4.5	The ANOVA analysis for response surface quadratic model	68

6

LIST OF FIGURES

Figu	re		Page
2.	1	The chemical structure of amylose	7
2.	2	The molecular structure of amylopectin	8
2.	3	Structure of lignocellulosic material	9
2.	4	The chemical structure of native cellulose	10
2.	5	The chemical structure of hemicellulose	11
2.	6	The chemical structure of lignin	12
2.	7	The schematic flowchart of sago starch extraction process	14
2.	8	The hydrogen price from different production process	18
3.	1	General experimental layout of this study	34
3.	2	The dried sago hampas	35
3.	3	The artificial neural network model	40
4.	1	The phylogenetic tree of the anaerobic biohydrogen-producing strain and it close relatives based on the almost complete 16s DNA sequence	54
4.	2	Biohydrogen production using 10 g/L of glucose by <i>Clostridium</i> butyricum A1 and <i>Clostridium</i> butyricum EB6	56
4.	3	The total accumulated of biohydrogen gas produced from sago hampas hydrolysate. <i>Clostridium butyricum</i> A1 and <i>Clostridium butyricum</i> EB6	58
4.	4	The total accumulated biohydrogen production from SPR hydrolysate by <i>Clostridium butyricum</i> A1 and <i>Clostridium butyricum</i> EB6	61
4.	5	Biohydrogen yield predicted by CCD.	69
4.	6	Three dimensional surface graphs of model for biohydrogen production at the optimum point	70
4.	7	The ANN model architecture for biohydrogen production.	71
() 4.	8	Biohydrogen production predicted by ANN.	72

LIST OF ABBREVIATIONS

A.	Aspergillus
ADF	Asperginus Acid Detergent Fiber
ADE	
	Acid Detergent Lignin
	Artificial Neural Network
ANOVA	Analysis of Variance
BLAST	Basic Local Alignment Search Tool
BOD	Biological Oxygen Demand
BPNN	Back Propagation Neural Network
Btu	British Thermal Unit
C.	Clostridium
CCD	Central Composite Design
CCS	CO ₂ Capture and Storage
CDW	Cell Dry Weight
CH ₄	Methane
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
COD	Chemical Oxygen Demand
DAS	Department of Agricultural Sarawak
DNA	Deoxyribonucleic Acid
DNS	3,5-Dinitrosalicylic Acid
dNTPs	Deoxyribonucleotide triphosphates
E.	Enterobacter
E.	Escherichia
EC	Enzyme Commission
EIA	Environmental Impact Assessment
GC	Gas Chromatography
g	G force
h	Hour
H ₂	Hydrogen
H_2S	Hydrogen Sulphite

HCI	Hydrochloric Acid
HHV	Higher Heating Value
HPLC	High Performance Liquid Chromatography
HRT	Hydraulic Retention Time
j	Jam
MgCl ₂	Magnesium Chloride
min	Minute
NaOH	Sodium hydroxide
NCBI	National Center for Biotechnology Information
NDF	Neutral Detergent Fiber
OPDC	Oil Palm Decantor Cake
OPEFB	Oil Palm Empty Fruit Bunches
PCR	Polymerase Chain Reaction
PDA	Potato Dextrose Agar
POME	Palm Oil Mill Effluent
PSA	Pressure Swing Adsorption
R ²	Correlation coefficient
RCM	Reinforced Clostridia Medium
rDNA	Ribosomal DNA
rpm	Rotation Per Minute
RSM	Response Surface Methodology
RSS	Residual Sum of Square
SAS	Sarawak Agriculture Statistic
sp.	Species
SPR	Sago Pith Residue
SRM	Steam Reforming of Methane
TKN	Total Kjedahl Nitrogen
UPM	Universiti Putra Malaysia
VFA	Volatile Fatty Acid
VSS	Volatile Suspended Solid
	-

CHAPTER 1

INTRODUCTION

Biohydrogen gas produced through fermentation process is an ideal alternative energy carrier that can be used as biofuel, due to it characteristics which are clean and sustainable bioenergy for the future. Biohydrogen is a simple gas with a molecular formula of H_2 and has high energy yield of 122 kJ/g, which is 2.75 times higher than fuels derived from petroleum (Claassen *et al.*, 2010; Chong *et al.*, 2009a; Pattra *et al.*, 2008). The combustion of hydrogen in engine as energy carrier is 50–70% more efficient than gasoline, hence the only byproduct generated is water (Pattra *et al.*, 2008; Fields, 2003), thus subsequently reduce the release of carbon dioxide into the atmosphere.

At present, the industrial production of hydrogen is through several processes including steam reforming of methane, electrolytic (water electrolysis) and thermochemical reactions (Levin and Chahine, 2010; Steinfeld, 2005). The major problems among these available technologies are ineffective cost and high energy consumption. Therefore, this situation leads to edge novel hydrogen uncompetitive to replace our current reliance on fossil fuel. Hence, innovative and novel biohydrogen production via fermentation using cheap feedstock has now being attempted because, it needs less land for set up and not being affected by weather conditions (Ni *et al.*, 2007).

In European countries, the "hyvolution" concept has been introduced in order to attain greener biohydrogen production. The concept is by exploiting bacteria that are capable in producing biohydrogen as byproduct during growth on biomass (Claassen *et al.*, 2010). Besides, utilization of biomass as a fermentation feedstock can reduce the cost of raw material which contributed around 50–70% of total biohydrogen production cost. By this mean, it will also help biomass related industries in managing their biomass waste and to generate extra profit (Hassan *et al.*, 2004).

Naturally, biomass present in various forms, including starch and lignocellulosic materials. The starch based biomass is composed of mainly starch, while the lignocellulosic biomass which is composed of 38-50% cellulose, 23-32% hemicellulose and 15-25% lignin (Perego and Bianchi, 2010). The polysaccharides of starch, cellulose and hemicellulose can be converted into simple sugars which are useful to be utilized as carbon sources for the fermentation process by microorganism. The bioconversion of biomass into simple sugars can be conducted through the hydrolysis process using specific enzyme. Utilization of carbon source recovered from the hydrolysis of biomass for biohydrogen production has been reported by several researchers including from palm oil mill effluent (Chong *et al.*, 2009a), oil palm empty fruit bunch (Inayat *et al.*, 2012), cassava wastewater (Sreethawong *et al.*, 2010) and sweet potato starch residue (Yokoi *et al.*, 2001) by exploiting various species of microorganisms.

Malaysia is blessed with favorable climate and abundant natural resources for commercial cultivation of crops such as sago palm. The Malaysian sago palm industry is one of the most important sago exporters in the world and exporting in the range of 55,000 to 65,000 tons/year of sago starch (Department of Statistic, Sarawak, 2012). The Department of Agriculture Sarawak (2010) has reported that the export value is increasing by 15–20% per year. In preliminary 2012, the export value of sago products was 48,314 tons compared to 2003 (40,780 tons) (Department of Statistic, Sarawak, 2012). Increment in production will significantly increase the number of waste generated from this industry, which may cause waste management problems and contribute to the environmental pollution. This industry has generated vast amount of wastes in the form of byproducts including sago bark, sago *hampas* and sago wastewater.

Sago *hampas* contains (on a dry weight basis) 58% starch, 23% cellulose, 9.2% hemicellulose and 3.9% lignin (Awg-Adeni *et al.*, 2012; Linggang *et al.*, 2012; Ozawa *et al.*, 1998). The enzymatic conversion of starch present in sago *hampas* into glucose produces another biomass which is known as sago pith residue (SPR). Linggang *et al.* (2012) has reported that SPR composed of (on a dry weight basis) 37% cellulose, 20% hemicellulose and 6% lignin and cellulose and hemicellulose can be hydrolyzed into a mixture of fermentable sugars using enzyme called cellulase. These types of biomass have the potential to be used as a carbon source in the production of valuable products. Thus, a study on the utilization of sago *hampas* and SPR for biohydrogen production was conducted. A new local isolated strain *Clostridium butyricum* A1 was employed to convert fermentable sugars into biohydrogen to be compared with a biohydrogen producer, *Clostridium butyricum* EB6 isolated by Chong *et al.* (2009a).

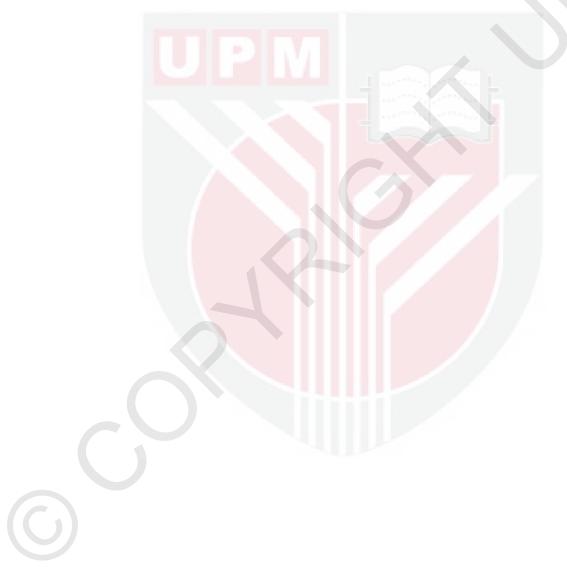
A variety of biohydrogen-producing microorganisms has been documented by several studies. To date, *Clostridium* sp. is widely employed for biohydrogen production since this species is capable in converting hexose sugar to biohydrogen with a theoretical yield of 4 mol H₂/mol hexose. This is higher than the biohydrogen produced by Enterobacter sp. that has a yield of 1 mol H_2 /mol hexose (Kotay and Das, 2008). However, several studies have been done for Enterobacter sp. since this species can achieve higher productivity than other reported species (Prasertsan et al., 2009; Kotay and Das, 2008; Chen et al., 2005). Jamil et al. (2009) has been reported on production of biohydrogen by Rhodopseudomonas palustris PBUM001 with biohydrogen yield 0.66 mL H₂/mL POME. Clostridium sp. has the capability to produce a biohydrogen yield in the range of 1.4–2.8 mol H₂/mol glucose (Levin and Chahine, 2010; Lin and Tanaka, 2006; Chen et al., 2005). The highest biohydrogen yield reported was 3.26 mol H₂/mol glucose by employing C. butyricum (Keskin and Hallenbeck, 2012). There are also several reports on the production of biohydrogen by Thermotoga sp. using biomass as substrate with a yield in the range of 1.1–2.0 mol H₂/mol glucose or other hexoses (Mars et al., 2010; Evvyernie et al., 2001).

However, biohydrogen production depends on various fermentation factors that correlate each other to improve biohydrogen yield. Due to the fact that, different substrate and Clostridia species employed in the fermentation produces different yield of biohydrogen, thus a tool that evaluate various fermentation factors at one time with statistical analysis are usually practiced. One of the most widely implemented tools is the response surface methodology (RSM) over the last two decades. RSM is an approach that implies the statistical technique based on the crucial technique of duplication and randomization, thus makes the optimization study easier (Baskar *et al.*, 2008). Based on the review, RSM is an effective tool to manipulate the large number of variables, therefore many reports have been used RSM to improve fermentation condition (Balusu *et al.*, 2005; Ezhumalai and Thangavelu, 2010). This tool has proven its ability to improve the biohydrogen yield using POME as the substrate, as conducted by Chong *et al.* (2009a; 2009b).

The artificial neural network (ANN) which is more advance and powerful statistical analysis tool is also able to optimize the fermentation parameters including for biohydrogen fermentation. One of the advantages of ANN is less time is required for development of extensive experimentation (Morteza *et al.*, 2013). This situation is due to the fact that, it could be conducted with limited numbers of experiments to predict the degree of non-linearity. It is also capable of learning complex relationships without requiring the knowledge of the model structure (Mingzhi *et al.*, 2009). According to Dutta *et al.* (2004), the ANN is a superior and more accurate tool in terms of modeling technique as compare to RSM because ANN depicts the nonlinearity of the model. Although, ANN has no ability to estimate the model equation similar to RSM, it still is able to estimate the response based on the trained data (Baş and Boyacı, 2007).

The study aims to produce the biohydrogen from sago biomass by *Clostridium butyricum* A1 with the specific objectives as follows:

- 1. To evaluate the suitability of sago *hampas* and sago pith residue for biohydrogen production by local isolates.
- 2. To compare biohydrogen production by *Clostridium butyricum* A1 and *Clostridium butyricum* EB6 using selected sago biomass.
- 3. To optimize biohydrogen production from selected sago biomass by selected *Clostridium* sp. using artificial neural network.



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