UNIVERSITI PUTRA MALAYSIA

PRODUCTION OF GLUCOSE FROM MIXED OIL PALM BIOMASS USING HYDROTHERMAL PRETREATMENT

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By

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As the world second biggest palm oil producer, Malaysia has most of its agricultural land planted with oil palm (*Elaeis guineensis Jacq*.). In conjunction with that, various and bulky amount of oil palm biomass were produced from the plantations and mills which contained a high amount of lignocellulosic components. The conversion of oil palm biomass into a value added product such as glucose helps to reduce the abundance of oil palm biomass. However, the structure of the biomass is compact and tough to be broken down. Therefore, pretreatment process is required to open up the lignocellulosic structure for enzymatic reaction thus improving the production of glucose.

Hydrothermal pretreatment process is an effective and environmental-friendly process for biomass fractionation due to its ability to solubilize hemicellulose; open the lignocellulosic structure and contributes to self-association of water molecules to create hydronium ions that can turn water pH into acidic, thus increasing the efficiency of pretreatment. Previous studies were using individual biomass in various pretreatment processes had shown a great effect on glucose conversion. In this study, hydrothermal pretreatment process was tested on mixed oil palm biomass to accommodate the huge amount of biomass produced daily. The aims of this experiment are to determine the effectiveness of hydrothermal pretreatment towards the lignocellulosic composition of mixed oil palm biomass and also to improve the glucose yield from pretreated mixed oil palm biomass using *Acremonium* cellulase.

Different weight ratios of oil palm biomass mixture were treated, i.e. 1:1:1, 1:1:2, 1:2:1 and 2:1:1 of oil palm frond fiber: oil palm empty fruit bunch: oil palm mesocarp fiber (OPFF:OPEFB:OPMF), respectively. The individual and mixed biomass were then subjected to hydrothermal pretreatment with different severity factors (log R_0) of 3.37 – 3.96 using miniclave reactor. The individual samples were represented as a control to investigate the effectiveness of mixed samples.

The morphological structure was examined with scanning electron microscope, wide-angle x-ray diffraction, Fourier-transform infrared spectral analysis and Brunauer-Emmett-Teller surface area analyses to observe the structure of oil palm biomass before and after pretreatment. The compositional analysis results were obtained by following National Renewable Energy Laboratory (NREL) method using dilute acid hydrolysis. Enzymatic hydrolysis of untreated and treated individual and mixed oil palm biomass was performed using 10 FPU of *Acremonium* cellulase per g of biomass was studied. The enzymatic hydrolysis was conducted at 50˚C for 72 hours in shaking condition. *Acremonium* cellulase has endocellulase and β-glucosidase activities which converted cellulose into monosaccharides mainly glucose.

In conclusion, the hydrothermal pretreatment had shown positive feedback towards high cellulose amount (53.8 ± 0.4%) of 1:2:1 mixed ratio under 190˚C for 10 min. The highest glucose yield also produced from the same mixed ratio under the same condition at 99.0 ± 0.8% under oil palm biomass ratio of 1:2:1 (OPFF:OPEFB:OPMF). Besides, the mixed sample also showed an increment of 22% of glucose conversion increment compared to the individual sample.

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

PENGHASILAN GLUKOSA DARIPADA CAMPURAN BIOMAS KELAPA SAWIT MENGGUNAKAN PRARAWATAN HIDROTERMA

Oleh

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Sebagai pengeluar minyak sawit kedua terbesar di dunia, hampir keseluruhan tanah pertanian di Malaysia ditanam dengan kelapa sawit (*Elaeis guineensis Jacq*.). Justeru, pelbagai biomas kelapa sawit terhasil dengan jumlah yang banyak dari dari ladang dan kilang yang mempunyai jumlah lignoselulosa yang tinggi. Penukaran biomas kelapa sawit kepada produk bernilai tinggi seperti glukosa dapat membantu mengurangkan biomas kelapa sawit yang banyak. Akan tetapi, struktur biomas adalah padat dan sukar untuk dileraikan. Oleh yang demikian, proses prarawatan diperlukan untuk membuka struktur lignoselulosa bagi meningkatkan penghasilan glukosa.

Proses prarawatan hidroterma adalah proses yang berkesan dan mesra alam untuk memecahkan komponen biomas disebabkan keupayaannya untuk solubilisasi hemiselulosa, membuka struktur lignoselulosa dan menjadikan molekul air bersatu untuk menghasilkan ion hidronium yang boleh menukarkan pH air kepada berasid dan sekali gus meningkatkan kecekapan prarawatan. Kajian terdahulu menggunakan biomas secara individu dalam pelbagai proses prarawatan telah menunjukkan kesan yang baik terhadap penukaran glukosa. Dalam kajian ini, proses prarawatan hidroterma telah diuji berdasarkan biomas campuran bagi menampung jumlah pukal biomas yang dihasilkan setiap hari. Tujuan kajian ini adalah untuk memastikan keberkesanan prarawatan hidroterma terhadap komposis lignoselulosa biomas kelapa sawit campuran dan untuk meningkatkan hasil glukosa daripada biomas kelapa sawit campuran yang terawat menggunakan *Acremonium* selulase.

Campuran biomas kelapa sawit telah dirawat menggunakan kadar yang berbeza-beza iaitu 1: 1: 1, 1: 1: 2, 1: 2: 1 dan 2: 1: 1 terdiri daripada serat

pelepah kelapa sawit: serat tandan buah kosong kelapa sawit: serat mesokarp kelapa sawit. Individu dan campuran biomas telah melalui proses prarawatan hidroterma dengan faktor keterukan (log R_0) yang berbeza dari 3.37 - 3.96 menggunakan reaktor miniklaf. Individu biomas mewakili pembolehubah dimalarkan untuk memastikan keberkesanan sampel campuran.

Struktur morfologi setiap sampel sebelum dan selepas prarawatan telah diperiksa melalui analisa-analisa mikroskop elektron imbasan, belauan sinar-X sudut lebar, spektrofotometri inframerah ubah-Fourier dan kawasan permukaan Brunauer-Emmett-Teller. Hasil analisa komposisi lignoselulosa diperoleh dengan mengikuti kaedah National Renewable Energy Laboratory (NREL) menggunakan hidrolisis asid cair. Hidrolisis enzimatik telah dilakukan terhadap biomas yang tidak diprarawat dan diprarawat secara individu dan campuran dengan menggunakan 10 FPU *Acremonium* selulase bagi satu g biomas. Proses hidrolisis enzimatik dilakukan pada suhu 50˚C selama 72 jam dalam keadaan 120 putaran seminit penggoncangan. *Acremonium* selulase mempunyai aktiviti endoselulase dan β-glukosidasa yang memulihkan selulosa menjadi monosakarida yang merupakan glukosa.

Secara konklusinya, proses prarawatan hidroterma telah menunujukkan kesan positif terhadap jumlah selulosa yang tinggi (53.8 ± 0.4%) daripada nisbah campuran 1:2:1 pada 190˚C untuk 10 minit. Hasil penukaran glukosa tertinggi diperoleh pada keadaan yang sama sebanyak 99.0 ± 0.8% di bawah nisbah biomas kelapa sawit 1:2:1 (OPFF:OPEFB:OPMF). Di samping itu, campuran biomas kelapa sawit telah menunjukkan peningkatan sebanyak 22% penukaran glukosa berbanding sampel individu.

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LIST OF ABBREVIATIONS

AIL	Acid insoluble lignin
AIM	Agensi Inovasi Malaysia
ASL	Acid soluble lignin
C_5	Pentoses
C_6	Hexoses
CPO	Crude palm oil
FFB	Fresh fruit bunch
FGB	First-generation bioethanol
FPU	Filter paper unit
FPU/g	Filter paper unit per gram
FPU/mL	Filter paper unit per milliliter
G	Guaiacyl
Gal-glu-man	Galactoglucomannan
GHG	Greenhouse gas
gL^{-1}	gram per liter
Glu-man	Glucomannan
GNI	Gross national income
H	4-Hydroxyphenyl
H^+	Hydrogen ion
H_2SO_4	Sulphuric acid
H_3O^+	Hydronium ion
HMF	Hydroxymethylfurfural
HPLC	High performance liquid chromatography
IPCC	Intergovernmental Panel on Climate Change
ktoe	Thousand tonnes of oil equivalent
m^2g^{-1}	meter squared per gram
mg	Milligram
Mha	Million hectares
mL	milliliter
mm	Millimeter
MPa	Mega pascal
MT	Million tonnes
ND	Not detected
OPEFB	Oil palm empty fruit bunch
OPFF	Oil palm frond fiber
OPMF	Oil palm mesocarp fiber
OPT	Oil palm trunk
PKO	Palm kernel oil
PKS	Palm kernel shell
POME	Palm oil mill effluent
S	Syringyl
SGB	Second-generation bioethanol
T	Temperature
v/v	volume per volume
w/w	Weight per weight
µm	micrometer

CHAPTER 1

INTRODUCTION

1.1 Research Overview

In Malaysia, 12% of gross national income (GNI) comes from the agricultural industry. Oil palm contributes to the most up to 8% of GNI or more than 80 billion (AIM, 2012). Along with this value, a large amount of biomass also has been generated and became a major problem towards the environment, thus a proper plan needs to be constructed. As the oil palm biomass consists of lignocellulosic components (Goh et al., 2012; Hassan et al., 2013; Mahmud et al., 2013), therefore conversion of lignocellulosic components into value-added products were observed to be more practical. The lignocellulosic composition of oil palm biomass can be converted into sugars which can able to produce biofuels such as bioethanol (Abdullah et al., 2016).

Due to recalcitrant of the lignocellulosic structure, a suitable pretreatment is needed. There are several types of pretreatment which are physical, chemical, biological and combined pretreatment such as physicochemical. For physical pretreatment, mechanical particle-size reduction and thermomechanical extrusion were often used. The main purpose of mechanical pretreatment is particle size and crystallinity reduction, thus, help to increase targeted specific surface area and decrease the degree of depolymerization (Myat and Ryu, 2016). Although physical pretreatment did not involve any chemical and biological approach, yet it is high in energy consumption and particle-size alone is not enough to modify the structure for the enzyme attack. Thermomechanical extrusion had seen to be more effective as compared to the previous method for physical pretreatment as it combined heating, mixing and shearing, therefore physical and chemical could be changed after passed the extruder and enhanced the accessibility of cellulose to enzyme attack.

Combined pretreatment process such as physicochemical pretreatment involved physical and chemical changes in the substrate, for example, hydrothermal pretreatment, steam explosion, ammonia fiber explosion (Kumar et al., 2009). Hydrothermal pretreatment in a closed reactor increases the pressure inside, while hot water solubilizes hemicellulose and alters the lignin composition. Size of substrates also decreased due to autohydrolysis reaction of water. In this experiment, the hydrothermal pretreatment was chosen due to chemical-free and harmless towards the environment. During hydrothermal pretreatment process, the auto-ionization of water molecules made the solution became acidic and enhanced disruption of the lignocellulosic component. Hemicellulose is susceptible to heat, thus it solubilizes into the solution and acetyl bonds within hemicellulose and converts into acetic acid. Soluble inhibitor could be generated after the pretreatment process where a proper filtration and wash are required before performing the enzymatic hydrolysis to prevent low sugar conversion yield.

1.2 Problem Statement

The current issues on industrial production of glucose are recalcitrance of lignocellulosic component and also abundant of biomass produced daily, such as empty fruit bunches, fronds, and mesocarp fiber. Studies found that hydrothermal pretreatment can disrupt the compact and tough structure of lignocellulosic components, as well as hydrolyzing the hemicellulose and alter the lignin structure. This condition leaves cellulose fiber exposed and able to be penetrated by the enzyme. Production of glucose mainly comes from cellulose as the subunit for cellulose is glucose. Glucose conversion from lignocellulosic biomass can reduce the amount of bulky amount of oil palm biomass. Besides that, mixed biomass also proven can improve the production of sugar, for example, Ashraf et al. (2017) showed an increment of 26% glucose from green and woody biomass and Pereira et al. (2015) gave 55% sugar conversion from mixed sugarcane bagasse with straw and hops compared to bagasse only.

1.3 Objectives of The Study

The objectives of this study are:

1. To determine the effectiveness of hydrothermal pretreatment towards the lignocellulosic composition of mixed oil palm biomass
2. To improve the glucose yield from pretreated mixed oil palm biomass using *Acremonium* cellulase

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