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CONVERSION OF OIL PALM TRUNK TO SUGARS AND ORGANIC ACIDS BY SUB-CRITICAL WATER REACTION

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

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Chair: Shamsul Izhar Bin Siajam, PhD
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Oil palm trunk (OPT) aging more than 25 years is among the most abundant biomass producing millions of tonnes of OPT per year. These abandoned OPT are either felled and chipped to allow for quicker return of nutrients to the soil or killed with poison allow it to decompose naturally in the field. OPT is a bio resource that has a high potential for conversion to energy and value added products. Sub-critical water (sub-CW) has been gaining interest in the conversion of biomass to useful products and energy due to its unique features. The objectives for this study are to convert OPT into sugars and organic acids by subcritical water reaction, to determine the optimum time and temperature to produce maximum amount of sugars, and to study the decomposition of pure cellulose by sub-CW reaction and compare with the results of OPT. Two different ages of 21- and 35-year-old OPTs were used to choose the best OPT that produce high yield of sugar. Both OPTs were divided into top and bottom parts whereby the inner zone were used since it contain high moisture content. A reactor filled with OPTs and distilled water was immersed in oil or molten salt baths for the sub-CW reaction. The reaction was carried out at temperatures ranging between 100 and 370°C and reaction time from 1 to 20 min. The results revealed that the 21-year-old (OPT 21) produced the maximum yield of sugar and organic acids. The optimum conditions for the highest yield of total sugar were 0.41 kg/kg-dry OPT (240 °C, 5 min) and 0.77 kg/kg-dry OPT (220 °C, 5 min) in bottom and top part, respectively. Sub-CW treatment caused the hydrolysis to occur thus promoted the decomposition of hemicellulose and cellulose in OPT. The saccharides produced as a result of the hydrolysis of OPT21 were cellotriose, cellobiose, glucose, fructose, and xylose. In the bottom part, fructose has the highest yield of 0.099 kg/kg-dry OPT at 220 °C while in top part, glucose has the highest yield of 0.51 kg/kg dry OPT at 230 °C. Sugar degradation of OPT produced organic acids such as acetic acid, lactic acid and malic acid. Acetic acid produced the highest yield of 0.2 kg/kg-dry OPT and 0.16 kg/kg-dry OPT in bottom and top parts, respectively. The decomposition of pure cellulose by sub-CW reaction successfully explained that hydrolysis had occurred. Sub-CW reaction showed promising results in producing sugars and organic acids from decomposition of

waste OPT. The sugar yields from OPT by sub-CW can be further study to produce second generation of bioethanol as alternative in replacing fossil fuels.

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

PENGUBAHAN DARIPADA BATANG KELAPA SAWIT KEPADA GULA DAN ASID ORGANIK OLEH TINDAK BALAS AIR SUB-KRITIKAL

Oleh

HAZWANI BINTI ISHAK

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Batang pokok kelapa sawit (OPT) yang berusia lebih daripada 25 tahun adalah antara biojisim kelapa sawit yang paling banyak dihasilkan dengan berjuta-juta tan OPT setiap tahun. OPT yang terbiar ini sama ada ditebang dan dipotong kecil untuk membolehkan pulangan nutrien yang lebih cepat ke dalam tanah atau diracunkan dan dibiarkan mengurai secara semula jadi di lapangan. OPT adalah sumber bio yang berpotensi tinggi untuk mennghasilkan produk tambah nilai dan tenaga. Sub-kritikal air (sub-CW) telah mendapat perhatian dalam pengubahan biojisim kepada produk yang bernilai dan tenaga kerana ciri-ciri uniknya. Objektif kajian ini adalah untuk menukar OPT kepada gula dan asid organik mengikut tindak balas air subkrital, untuk menentukan masa dan suhu optimum untuk menghasilkan gula yang maksimum, dan untuk mengkaji penguraian selulosa asli oleh tindak balas sub-CW dan membuat perbandingan dengan hasil kajian OPT. Dua batang OPT yang berumur 21 dan 35 tahun digunakan untuk memilih OPT yang terbaik dalam menghasilkan kadar gula yang tinggi. Kedua-dua OPT dibahagikan kepada bahagian atas dan bawah di mana zon dalaman digunakan kerana ia mengandungi kandungan lembapan yang tinggi. Reaktor yang diisi dengan OPT dan air suling dibenamkan di dalam minyak atau garam cair untuk tindak balas sub-CW. Tindak balas dilakukan dalam linkungan suhu antara 100 dan 370 ° C dan masa tindak balas dari 1 hingga 20 minit. Hasil kajian menunjukkan bahawa batang 21 tahun (OPT 21) menghasilkan gula dan asid organik yang maksimum. Kondisi optimum untuk menghasilkan gula tertinggi ialah 0.41 kg / kg OPT kering (240 ° C, 5 min) dan 0.77 kg / kg OPT kering (220 ° C, 5 min) masing-masing di bahagian bawah dan atas. Rawatan sub-CW menyebabkan hidrolisis berlaku sehingga menggalakkan penguraian hemiselulosa dan selulose dalam OPT. Sakarida yang dihasilkan daripada hidrolisis OPT 21 adalah selotriosa, selobiosa, glukosa, fruktosa, dan xylose. Di bahagian bawah, fruktosa mempunyai hasil tertinggi sebanyak 0.099 kg / kg OPT kering pada suhu 220 ° C manakala di bahagian atas, glukosa mempunyai hasil tertinggi 0.51 kg / kg OPT kering pada 230 ° C. Degradasi gula dalam OPT menghasilkan asid organik seperti asid asetik, asid laktik dan asid malik. Asid asetik menghasilkan hasil tertinggi iaitu 0.2 kg / kg OPT kering dan 0.16 kg / kg OPT kering di bahagian bawah dan atas. Penguraian selulosa asli oleh tindak balas sub-CW berjaya menjelaskan bahawa hidrolisis telah berlaku. Tindak

balas sub-CW menunjukkan hasil yang memberangsangkan dalam menghasilkan gula dan asid organik daripada penguraian sisa OPT. Hasil gula dari OPT oleh sub-CW boleh terus dikaji untuk menghasilkan generasi kedua bioethanol sebagai alternatif penggantian bahan bakar fosil.

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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 of the Supervisory Committee were as follows:

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This is to confirm that:

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Sub-CW	Subcritical water
OPT	Oil Palm Trunk
OPT 21	21 years old oil palm trunk
OPT 35	35 years old oil palm trunk
TOC	Total organic carbon

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Oil palm trunk (OPT), scientifically known as *Elaeis guineensis*, is one of the most abundant biomass in Malaysia that has a high potential for producing value-added products. Originally from West Africa, it is utilized in the production of foodstuffs, wine, medicines, detergents, soap and cosmetics (Casson, 2003, Yamada et al., 2010). Since the late 1950s, oil palm has become one of the most widely planted commercial crops, whereby almost 80% of the world's oil palm plantations is focused on Southeast Asia for its edible oil. Malaysia and Indonesia are the world's leading exporters of palm oil (Murai & Kondo, 2011; Yamada et al., 2010).

A recent developments in conjunction with National Biomass Strategy 2020 have recognized the great potential of converting oil palm biomass into high value-added products. The biomass strategy also highlighted that there would be a substantial contribution to the country's gross national income (GNI) of about RM 30 billion by 2020 through full utilisation of the oil palm biomass (The Star Online, 2011).

Recently, there had been an increased interest in the utilisation of the oil palm biomass as an energy source. In addition to the production of glucose, OPT has been recently utilized in the production of bioethanol and bioplastics. Recent studies have shown to produce bioethanol by hydrolyzing the lignocellulose composition of OPT.

Sub-critical water (hereafter called sub-CW) has been gaining more interest recently in the conversion of unused biomass and organic materials to useful products and energy. It is defined as a water between its boiling point of 100 ˚C and its critical temperature of 374 ˚C under sufficiently high pressure to maintain the liquid state of water. Sub-CW has unique features such as a decrease in dielectric constant as temperature increase (Yoshida and Matsuzaki, 2014; Yoshida and Asghari, 2007). Low dielectric constant means the polarity of water changes thus making water to behave like a non-polar substance. This highlights the advantages of sub-CW over organic solvent extraction techniques that are environmentally undesirable. Besides, the value of the ion product shows a maximum at 250 °C that indicates sub-CW possesses strong hydrolysis power at around that temperature.

1.2 Problem Statement

The success of the oil palm industry in Malaysia is from the convergence of government and private sector strategies and policies. Despite the large production of palm oil, the yielded oil contributes to about 10% of the total biomass produced in the plantation. The remaining 90% comprises of the huge amount of oil palm wastes such as oil palm shells, mesocarp fibers, empty fruit bunch, oil palm fronds and oil palm trunks. Unfortunately, these remaining 90% biomass is disposed daily (in tonnes). Thus, the oil palm biomass can be utilised back to form high-end value products not only as a zero-waste plan but also as an energy source if it is developed in a right sustainable way.

Oil palm trunks (OPTs), which are produced more than 10.8 million tonnes annually (Goh et al., 2010), contribute to the high amount of oil palm waste in this country. As oil palm trees have an economic lifespan of approximately 25-30 years, thereafter the old trees are felled and replanted. Nowadays, most of the OPTs left in the plantation are used as fertiliser. The OPTs are felled and chipped for a quicker return of nutrients to the soil and poisoned to decompose naturally in the plantation site.

All the OPT waste can be utilized to convert into value-added products. Currently, only a small percentage of OPTs are used in the wood industry. The outer part and veneers are used in manufacturing plywood which is already commercialized. Similarly, the paper or pulp production and also feedstock such as animal feed pallet are other commercialized products from OPT (Agensi Inovasi Malaysia, 2013).

The inner part of OPT is not used since it contains high moisture content and easily rots. It is a bioresource which can be entirely converted into valuable chemicals and products. It consists of a high composition of lignocellulosic materials comprising 37.14% cellulose, 31.8% hemicellulose, 22.3% lignin, and 4.3% ash (Morad et al., 2015). The OPT lignocellulosic biomass contain huge quantities of sap and abundant of fermentable sugar which has great potential for bioethanol production. In recent years, biomass can meet demand as a renewable resource by less reliance on fossil fuel and also become alternative fuels to existing transport fuels besides reducing global warming effect to the environment. Furthermore, bioethanol production showed interesting features in commercializing industrial technologies for inexpensive and abundance OPT biomass (Rafidah J et al., 2011).

Hydrolysis of hemicellulose is recovered at temperatures between 160-230 °C and at higher saturated vapour pressure to make sure it is in the liquid phase (F. P. Cardenas-Toro et al., 2014; Prado et al., 2016). Hydrolysis of acetyl group in hemicellulose will form acetic acid together with pentose sugars such as xylose, arabinose, and galactose (Lin et al., 2015).

Cellulose is slightly hydrolysed in short reaction time and at temperatures below 230 °C to form oligosaccharides which further decomposed into monosaccharides (Prado et al., 2014). The monosaccharides degradation that forms organic acids such as formic acid, acetic acid, lactic acid, levulinic acid, and 5-HMF, which are the main products of sub-CW. Acetic acid is used in the manufacturing of plastics, coatings, paints and also solvents. Lactic acid is used in chemical industry and food industry as food preservatives

There are many studies on pre-treatment and extraction of value-added products from OPT such as enzymatic hydrolysis, hydrothermal hydrolysis, steam explosion, concentrated acid hydrolysis, ionic liquids, alkaline pre-treatment and supercritical CO_2 treatment. Nevertheless, the disadvantages of these conventional methods include tedious tasks, high energy consumption, expensive technology, poor extraction yield and high operating costs. Furthermore, some organic solvents or acids that are used in the conventional process are toxic chemicals that can cause an explosion and environmental pollution.

The sub-CW process uses water as a solvent making it environmentally safe and non-toxic. No pre-treatment (crashing and drying) of biomass is required while using sub-CW. The presence of water at high temperatures as a reactant leads to hydrolysis reactions whereby lignocellulosic materials are hydrolysed into soluble oligo-, di-, and monosaccharides. Some of the lignocellulose is decomposed into organic acids (Salak & Yoshida, 2010).

Currently, sub-CW has been used for hydrolysis of biomass and carbohydrates to sugars and other valuable products. Salak & Yoshida, (2010) have investigated the chemical hydrolysis of Japanese red pine wood and pure cellulose using sub-CW in the presence and absence of an acid catalyst. Sasaki et al. (Sasaki et al., 1998) have studied the decomposition of cellulose using sub-CW and supercritical water reactions to recover glucose, fructose and oligomers in the temperature range 290 to 400 °C at 25 MPa with a flow type reactor.

Despite many researchers had utilised oil palm biomass such as mesocarp, oil palm frond (OPF), oil palm fruit press fibres (FPF), and empty fruit brunch (EPB) (Mustapa et al., 2011, Mazaheri et al., 2010, Hanim et al., 2012, Kurnin et al., 2016) under sub-CW conditions, there is no study or research yet on OPT by using sub-CW method. Thus, this study focused on the conversion of OPT to value-added products with emphases on the sugar and organic acid in the lignocellulose portion by using sub-CW hydrolysis reaction by varying reaction temperature and reaction time.

1.3 Research Objectives

There is a potential to use sub-CW for conversation and decomposition of OPT to valuable materials. Most methods used in this research were based on previous sub-CW studies led by Professor Yoshida with some alterations and modifications.

The objectives of this research are:

1. To analyse the composition of hemicellulose and cellulose in OPT, and its conversion into sugars and organic acids soluble in water-phase by sub-critical water hydrolysis reaction,
2. To determine the optimum time, temperature, age and part of OPT to produce the maximum amount of sugars, and
3. To justify the cellulose decomposition in pure cellulose and in OPT and compare the results.

1.4 Scope and Limitation

The raw material used in this study is oil palm trunks (OPTs) aged 21 and 35 years old whereby the top and bottom parts of OPT is used in this research. It is chosen because of abundantly available biomass waste in Malaysia. A survey of literature on OPT reported on various sugar extraction methods, alcohol fermentation and etc.. To our knowledge, no research has been carried out on sub-CW hydrolysis reaction of OPT. This research work is limited to study the sub-CW hydrolysis of OPT and to analyse the extracted value-added products. Therefore, this study aims to analyse the lignocellulose in OPT and examine the effects of temperature (100-250 °C) and time (1-20 min) by sub-CW. Furthermore, this study compares pure cellulose and cellulose in OPT using the sub-CW reaction. This work focussed on the hydrolysis capability of sub-CW although it is also known that sub-CW possesses good activity to promote pyrolysis and oxidation at high temperature. This research work is conducted at the Process Control and Instrumentation Laboratory (Block J 2.4), Faculty of Engineering, UPM.

1.5 Thesis Layout

The overall research work is organized into five chapters in this thesis.

Chapter 1 discusses the obstacles and current scenario of the oil palm biomass in Malaysia together with overcome the problems. The objectives of this research are proposed in this chapter.

Chapter 2 reports numerous previous studies exploring the potential of OPTs by identifying and articulating the composition of OPT in extracting value-added products. Besides that, the various applications of the subcritical water as a new green technology of chemical engineering are also reviewed.

Chapter 3 deals with the materials and methods. The OPT sample preparation, the sub-CW reactor setup, the sub-CW hydrolysis reaction, analytical methods of the water-soluble phase components and composition of OPT are further explained.

Chapter 4 provides the results and discussions of the research. The effect of temperature (over the whole range of sub-CW) and time course on the decomposition of OPT (hemicellulose and cellulose) to sugars are investigated. The optimum temperature and time to produce the maximum amount of sugars are presented. The plausible explanations for these findings are discussed in detail.

Chapter 5 summarises the conclusion and recommendations of the research. The overall important results, as well as some recommendations for the improvement of the results or methodology, are stated.

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