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OPTIMISATION OF SECOND STAGE DILUTE ACID HYDROLYSIS OF OIL PALM FRONDS INTO GLUCOSE

SOHEIL NEKOUI

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OPTIMISATION OF SECOND STAGE DILUTE ACID HYDROLYSIS OF OIL PALM FRONDS INTO GLUCOSE

By

SOHEIL NEKOUI

Thesis Submitted to the School of Graduate Studies,
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This thesis is dedicated to
my beloved parents
for their love, endless supports and encouragement with love

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

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Chairman **:Professor Robiah Yunus, PhD**

Faculty **:Engineering**

In this study, the potential of OPF as a lignocellulosic feedstock to produce fermentable sugars using two-stage dilute-acid hydrolysis was assessed. The proximate analysis revealed that OPF fibre was composed of 32.93% cellulose, 29.91% hemicellulose and 19.53% lignin. This study focused on the hydrolysis of cellulose fraction of OPF into glucose in the second-stage of two-stage dilute acid hydrolysis. The second stage reactions were carried out above 150 °C. Four parameters that affect the yield of glucose, namely acid concentration, reaction temperature, reaction time and liquid to solid ratio were investigated. The batch reactions were carried out under different operating conditions as proposed by the experimental design generated by the Response Surface Methodology (RSM). The RSM was used to determine the optimum point for the second stage dilute acid hydrolysis process. In the first stage of dilute acid hydrolysis 4.33 g/L (33% yields) glucose was recovered. From the second stage hydrolysis, at optimum condition of 150 °C temperature, 6 % sulphuric acid concentration, 62 min of reaction time and a liquid/solid ratio of 28:1, the glucose yield was 4.48 g/L (34%). The amount of generated inhibitor (HMF and furfural) was 0.22 g/l. The total glucose yield from both stages of the two-stage hydrolysis process under optimum conditions was 67%.

The kinetics study on the formation of glucose from dilute acid hydrolysis of OPF revealed that the reaction was a first order irreversible reaction. Based on the values of rate constants, it was found that the rate of formation of glucose (k_1) was more dominant than the rate of degradation (k_2). The activation energy values at the optimum acid concentration of 6% were 85.733 kJ/mol for glucose formation and 123.238 kJ/mol for glucose degradation. The n value for glucose formation at 150 °C was 0.647 while for glucose degradation was at 0.487. The findings of this study suggest that the glucose yield can be increased while the inhibitor formation can be decreased by increase in acid concentration and decrease in reaction temperature.

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

PENGOPTIMUMAN TAHAP KEDUA HIDROLISIS ASID CAIR PELEPAH KELAPA SAWIT KEPADA GLUKOSA

Oleh

SOHEIL NEKOUI

Oktober 2014

Pengerusi : Professor Robiah Yunus, PhD

Fakulti : Kejuruteraan

Dalam kajian ini potensi pelepah kelapa sawit sebagai bahan mentah untuk menghasilkan lignoselulosa gula beragi menggunakan dua peringkat hidrolisis asid-cair dinilai. Analisis proksimat mendedahkan bahawa serat pelepah kelapa sawit terdiri daripada 32.93% selulosa, 29.91% hemiselulosa dan 19.53% lignin. Itu, kajian ini memberi tumpuan kepada hidrolisis pecahan selulosa daripada pelepah kelapa sawit menjadi glukosa dalam peringkat kedua bagi dua peringkat hidrolisis asid-cair. Tindakbalas peringkat kedua telah dijalankan di atas suhu 150 °C. Empat parameter yang memberi kesan kepada hasil glukosa, iaitu kepekatan asid, suhu, masa tindak balas dan nisbah cecair kepada pepejal telah disiasat. Reaksi 'kelompok' telah dijalankan di bawah keadaan operasi yang berbeza seperti yang dicadangkan oleh reka bentuk eksperimen yang dihasilkan oleh rekabentuk metodologi tindakbalas permukaan (RSM). RSM ini digunakan untuk menentukan titik optimum untuk peringkat kedua hidrolisis asid-cair. Peringkat pertama hidrolisis asid-cair telah menghasilkan glukosa sebanyak 4.33 g/L (33% yield). Daripada hidrolisis asid peringkat kedua, pada keadaan suhu optimum 150 °C, 6% kepekatan asid sulfurik, 62 minit masa tindak balas dan nisbah cecair / pepejal 28:1, hasil glukosa adalah 4.48 g/L(34 % yield). Jumlah perencat (HMF dan furfural) yang dihasilkan adalah 0.22 g/L. Jumlah hasil glukosa daripada kedua peringkat proses hidrolisis dua peringkat pada keadaan optimum adalah 67%.

Kajian kinetik kepada pembentukan glukosa daripada hidrolisis asid-cair pelepah kelapa sawit mendedahkan bahawa reaksi itu adalah kadar pertama reaksi tidak boleh diubah. Berdasarkan nilai pemalar kadar, didapati bahawa kadar pembentukan glukosa (k_1) adalah lebih dominan daripada kadar degradasi (k_2). Nilai tenaga pengaktifan pada kepekatan asid optimum 6% adalah 85.733 kJ/mol untuk pembentukan glukosa dan 123.238 kJ/mol untuk degradasi glukosa. Nilai n untuk pembentukan glukosa pada 150 °C adalah 0.647 manakala bagi degradasi glukosa adalah pada 0.487. Hasil kajian ini mencadangkan bahawa hasil glukosa boleh

ditingkatkan manakala pembentukan perencat boleh dikurangkan dengan peningkatan dalam kepekatan asid dan pengurangan suhu tindakbalas.

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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:

Robiah Yunus, PhD
Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Said Salah Elnashaie, PhD
Professor
Faculty of Engineering
Universiti Putra Malaysia
(Member)

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

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Supervisory
Committee: ______________________

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LIST OF ABBREVIATIONS

OPF	Oil Palm Frond
LSR	Liquid solid Ratio
RSM	Response Surface Methodology
HPLC	High-performance liquid chromatography
TGA	Thermogravimetric Analysis
SEM	Scanning Electron Microscope
EDX	Energy-dispersive X-ray spectroscopy
HMF	Hydroxymethylfurfural
NDF	Neutral Detergent Fibre
ADF	Acid Detergent Fibre
ADL	Acid Detergent Lignin
SST	Total Sum of Square Error
SSE	Sum of Square Error
ANOVA	Analysis of variance
DF	Degree of Freedom
C.V	Coefficient of Variation

CHAPTER 1

INTRODUCTION

1.1 Background

Due to fluctuation in price of petroleum, limited fossil fuel reserve and growing concern associated with the environmental impact of fossil fuel, the current research attention is driven towards finding alternative non-fossil fuels for the transportation sector. An alternative fuel must be readily available, environmentally acceptable, economically competitive and technically feasible (Meher *et al.*, 2006).

Biomass-based fuel is known as biofuel. Biofuels are the potential candidate for alternative "green" energy substitute for fossil fuels (Demirbas, 2009). Currently biodiesel and bioethanol are two main renewable liquid fuels for the transportation sector, which could substitute for diesel and gasoline fuels (Demirbas, 2008). The advantages of biomass-based fuels are as following: (1) they reduce the greenhouse gases (GHG) emissions, (2) They are easily produced from common organic resources, (3) they represent a CO_2-cycle within combustion, (4) They are biodegradable and contribute to sustainable development (Demirbas, 2008).

Bioethanol is a grain-based alcohol, scientifically known as ethyl alcohol EtOH or C_2H_5OH (Balat, 2011). It can be produced synthetically from crude oil or by microbial process of biomass resources via fermentation process. Compared to gasoline, ethanol provides a larger octane number (108), wider flammability limit and faster flame speed (Balat *et al.*, 2008). In 2011, global bioethanol production reached a record of 22.356 million gallons (AFDC, 2013). The US and Brazil are the world's largest producers of biofuel, together providing around 90% of the biofuel production exploiting corn and sugarcane respectively (Limayem and Ricke, 2012).

Bioethanol is currently being used as an additive in gasoline formulation usually at concentration of 10% bioethanol to 90% gasoline (E10). It is commonly known as "gasohol" which provides higher octane and cleaner emissions compared to gasoline. E10 could be applied in all conventional engines without any engine modification. This blend could also be utilized at a higher concentration, if the engine is modified, for example, E85 (Balat and Balat, 2009). Some countries have employed bioethanol program such as the Brazil (E20, E25, and any blend), United States (E10 and E85), Canada (E10 and E85) and Australia (E10) (Balat *et al.*, 2008).

Bioethanol can be produced from various feedstocks containing fermentable sugars after which will be metabolized by different microorganisms. Two types of feedstocks are mostly utilized globally in the last decades: sugar cane and corn starch, particularly in regions like Brazil and United States. The production of bioethanol from these sources is controversial because of the food versus fuel issues. These raw materials have been used historically as food for humans and as feed for animals. Thus, using these feedstocks for fuels will disturb the food supply and may trigger sharp increase in food prices.

The bioethanol derived from the edible source is known as the first-generation bioethanol (FGB) (Goh *et al.*, 2010b). In order to minimize the controversy associated with these food-grade feedstocks for bioethanol production, attention have been shifted towards lignocellulosic materials as feedstock for bioethanol production (Tye *et al.*, 2011). The bioethanol generated from these lignocellulosic feedstocks is known as second-generation bioethanol (SGB) (Goh *et al.*, 2010b). The use of these feedstock has been currently extended to several countries worldwide, such as China, India, Australia, Canada and many others (Balat, 2011).

Since the beginning of 1970, palm oil industry has been one of the most important industries in Malaysia (Alam and Ainuddin, 2007). Malaysia has emerged as one of the top producers and exporters of palm oil, which account for 89% of global exports and 47% of the current global palm oil production (Sabiha-Hanim *et al.*, 2011). In Malaysia, major proportions of agriculture waste come from oil palm cultivation, in the form of chopped trunks, shell and fibres, empty fruit bunch (EFB) and oil palm fronds (OPF) (Sumathi *et al.*, 2008). Oil palm frond amounts to 70% of the total oil palm cultivations waste in Malaysia (Alam and Ainuddin, 2007). It is reported that each hectare of oil palm plantation generates 10.88 tons of dead fronds as a by-product. These wastes constitute biomass in the form of lignocelluloses, celluloses and hemicellulose which are suitable for bioethanol production (Kelly-Yong *et al.*, 2007)

Lignocellulose biomass is composed of cellulose, hemicellulose and lignin. This complex is resistant against many chemical and microbial attacks (Balat *et al.*, 2008). Typically, oil palm fronds contain a high portion of cellulose and the lower percentage of lignin (Kim *et al.*, 2003). There are four main process steps in the production of bioethanol from lignocellulosic biomass: pre-treatment, hydrolysis, fermentation and distillation (Balat, 2011). A cost effective bioethanol production is highly dependent on the availability of cheap feedstock and plant operability (Alvarado-Morales *et al.*, 2010). Lignocellulosic feedstock is considered as the cheapest raw material for bioethanol production (Goh *et al.*, 2010a).

Currently, acid hydrolysis and enzymatic hydrolysis are the most common hydrolysis processes for lignocellulosic biomass (Balat, 2011). Dilute acid hydrolysis is a simple and fast process in which acid recovery is not needed after this process(Conde-Mejía *et al.*, 2012; Hu *et al.*, 2010) .However, dilute acid hydrolysis is recommended to be carried out in two stages in order to avoid sugar degradation and generation of inhibitors, at high temperature. In the first stage, hemicellulose in relatively mild condition is converted to 5-carbon sugars, which is sometimes considered as the pre-treatment step. In the second stage, cellulose in the residual solid is hydrolyzed under more harsh condition to 6-carbon sugar. (Karimi *et al.*, 2006; Taherzadeh and Karimi, 2007a)

1.2 Problem Statement

Currently, a large amount of OPF is mainly disposed by burning or direct decaying in the environment. Only a small amount is converted into compost. These activities lead to serious environmental problems(Sheh *et al.*, 2013). Production of bioethanol from this low cost biomass is a promising alternative to convert the waste into useful products (Goh *et al.*, 2010b). However, the hydrolysis of lignocellulosic biomass to fermentable sugar prior to converting to bioethanol has been the major hurdles. Many attempts have been made by researchers to improve the hydrolysis of lignocellulosic materials such as OPF. Hence different hydrolysis techniques have been proposed in order to combat this problem. Based on the literature, there is little information on the hydrolysis of OPF via dilute acid hydrolysis. However, Amirkhani *et* al.(2014) have successfully developed the optimum process for the first stage of the two-stage dilute acid hydrolysis of OPF. They managed to convert almost 94% of potential xylose in the OPF at 120°C using 2% acid. Nevertheless, their study only optimized the conversion of OPF to xylose and only a small percentage of glucose was present in the sugar solution. Hence, a large percentage of lignocellulosic components in OPF namely cellulose has yet to be hydrolyzed. This process will only can take place at higher acid concentration and higher temperature. In this study, the processing conditions for the second stage of the two-stage dilute acid hydrolysis of OPF will be explored for optimum glucose recovery.

1.3 Research Objective

Among the chemical hydrolysis techniques dilute acid hydrolysis is considered as the most widely utilized process in the hydrolysis of lignocellulosic wastes. Oil Palm Frond *(OPF)* fibre contains high cellulose and hemicellulose content, thus a potential feedstock for simple sugars production. The overall objective of this study is to evaluate the two-stage dilute-acid hydrolysis process to convert the cellulose portion of OPF fibre to simple sugars predominantly glucose.

The specific objectives of this thesis are listed below.

1) To optimize the second-stage dilute acid hydrolysis for maximum glucose recovery.
2) To perform the kinetics study of the second stage hydrolysis.

Two-stage dilute acid hydrolysis is an effective method for hydrolysis of lignocellulosic material. The scope of this research emphasizes on the hydrolysis of cellulose fraction of OPF into glucose in the second-stage of two-stage dilute acid hydrolysis using a pressurized-batch reactor. The second stage reactions were carried out above 150 °C. In this study, the acid concentration, temperature, time and liquid to solid ration are process parameters investigated in the second stage of two-stage dilute acid hydrolysis.

1.4 Thesis Outline

This thesis consists of five chapters. Chapter one introduces the research background, problem statement and objectives of the study. Chapter two presents the detailed literature review associated with bioethanol, lignocellulosic biomass, and different technologies for hydrolysis process. Chapter three describes the materials and the methodology involved in this study. The analytical methods, including characterization and testing procedures for the determination of sample composition, the design and analysis of experiments and the experiments of hydrolysis procedures are discussed in this chapter. Discussions on data analysis and interpretation are presented in chapter four. Finally, the conclusion for the objectives, recommendations and suggestions for further work is presented in chapter five.

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