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MICROWAVE ASSISTED PRETREATMENT AND ENZYMATIC HYDROLYSIS FOR SUGAR PRODUCTION FROM SAGO PALM BARK

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By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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February 2017

Chairman : Rozita Bt. Omar, PhD
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Sago palm bark (SPB) is lignocellulosic biomass feedstock and a by-product of starch industry in Malaysia. The complex structure of lignocellulosic materials makes it resistant to enzymatic hydrolysis. Current technologies including physical and chemical pretreatment methods result in relatively low sugar yields, severe reaction conditions and high processing costs. A green and low energy pretreatment process is proposed using microwave irradiation. SPB was subjected to microwave-assisted pretreatment to assess the effects of pretreatment using diluted acid and alkaline solvents on sago palm bark characteristics and inhibitor formation. The effects of microwave-assisted pretreatment parameters (operating conditions) was also evaluated on glucose and xylose yield via enzymatic hydrolysis. Additionally, an estimation model for glucose and xylose yield from the enzymatic hydrolysis of SPB based on microwave-assisted pretreatment conditions was developed.

The microwave-assisted pretreatments utilized three solvents which are 0.1 N H_2SO_4 (MSA), 0.1 N NaOH (MSH), and 0.01 N $NaHCO_3$ (MSB). The microwave-assisted methods were compared to conventional heating pretreatment. The experimental design was done using a response surface methodology (RSM) and Box Bekhen Design (BBD) was used to evaluate the main and interaction effects of the pretreatment parameters on glucose and xylose yield obtained after the enzymatic hydrolysis step. The pretreatment parameters ranged from 5-15% solid loading (SL), 5-15 minutes of exposure time (ET) and 80-800 W of microwave power (MP). The enzymatic hydrolysis was carried out using 24 FPU/g of cellulase, 2 UN/g of xylanase and 50 U/g of β-glucosidase. An estimation model for glucose and xylose yield from the enzymatic hydrolysis of SPB was developed by using artificial neural network (ANN) and particle swarm optimization (PSO). The above-mentioned artificial intelligent systems were combined to form a hybrid PSO–ANN model.

The MSA pretreatment resulted in higher lignin and hemicellulose degradation giving more porous structure of SPB compared to microwave-assisted alkaline and conventional pretreatments. No degradation products such as furfural, acetic acid and

HMF were found in MSA pretreatment liquor. Conversely, conventional pretreatment using 0.1 N H_2SO_4 produced 0.47 mg/ml of acetic acid. After the enzymatic hydrolysis steps, it is revealed that the microwave-assisted pretreatment methods resulted in a higher sugar yield than conventional pretreatment methods. The results also show that the pretreatment parameters played a crucial role in the trend of the glucose and xylose yield from enzymatic hydrolysis of SPB. The results of glucose and xylose yield from MSA pretreatment and enzymatic hydrolysis of SPB were selected to develop a hybrid PSO–ANN model. The hybrid PSO–ANN model showed a higher regression coefficient (R^2) for the estimation and the experimental values of glucose and xylose at 0.9939 and 0.9479, respectively. Meanwhile, R^2 values of the RSM model were only 0.8901 and 0.8439 for glucose and xylose, respectively.

This study concluded that the SPB has the potentials to be developed as future fermentable sugars source and the microwave-assisted pretreatment would be a possible route to enhance the release of these sugars.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

PRA-RAWATAN BERBANTU GELOMBANG MIKRO DAN HIDROLISIS ENZIMATIC UNTUK PENGELUARAN GULA DARI KULIT POKOK SAGU

Oleh

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Sago kulit sawit (SPB) adalah lignoselulosa bahan mentah biojisim dan hasil sampingna industri kanji di Malaysia. Struktur kompleks bahan lignoselulosa menjadikannya tahan hidrolisis enzim. Teknologi terkini termasuk kaedah pra-rawatan fizikal dan kimia menghasilkan produk gula yang rendah, keadaan tindak balas yang teruk dan kos pemprosesan yang tinggi. Proses pra-rawatan hijau dan bertenaga rendah dicadangkan dengan menggunakan sinaran gelombang mikro. SPB dipra-rawat menggunakan gelombang mikro untuk menilai kesannya menggunakan asid dan alkali cair kepada ciri SPB dan penghasilan perencat. Kesan pembolehubah pra-rawatan berbantu gelombang mikro (keadaan operasi) juga dinilai pada penghasilan glukosa dan xilosa setelah melalui proses enzim hidrolisis. Selain itu, model anggaran glukosa dan xilosa yang terhasil daripada hidrolisis enzim SPB berdasarkan keadaan pra-rawatan yang dibantu oleh gelombang mikro telah dibangunkan.

Pra-rawatan gelombang mikro tersebunt menggunakkan tiga pelarut iaitu 0.1 N H_2SO_4 (MSA), 0.1 N NaOH (MSH) dan 0.01 N $NaHCO_3$ (MSB). Metod berbantu gelombang mikro ini telah dibandingkan dengan pra-rawatan menggunakan pemanasan konvensional. Reka bentuk eksperimen telah dibuat menggunakan Metodologi Balas Permukaan (RSM) dan Box Bekhen Design (BBD) telah digunakan untuk menilai kesan utama dan interaksi parameter pra-rawatan kepada glukosa dan xilosa yang terhasil selepas proses hidrolisis enzim. Parameter pra-rawatan adalah antara 5-15% muatan pepejal (SL), 5-15 minit masa pendedahan (ET), dan 80-800 W kuasa gelombang mikro (MP). Hidrolisis enzim telah dijalankan dengan menggunakan 24 FPU/g selulase, 2 UN/g xilanase dan 50 U/g β-glukosidase. Model anggaran untuk hasil glukosa dan xilosa daripada hidrolisis enzim SPB berdasarkan keadaan pra-rawatan berbantu gelombang mikro telah dibangunkan dengan menggunakan rangkaian neural tiruan (ANN) dan zarah kumpulan pengoptimuman (PSO). Sistem kepintaran buatan yang disebut di atas telah digabungkan untuk membentuk satu model PSO–ANN hibrid.

Pra-rawatan MSA menyebabkan degradasi lignin dan hemiselulosa yang lebih tinggi dan mnghasilkan struktur SPB yang lebih poros berbanding pra-rawatan alkali dan pra-rawatan secara konvensional. Tiada produk degradasi seperti furfural, asid asetik dan HMF ditemui di dalan produk cecair selepas pra-rawatan MSA. Sebaliknya, pra-rawatan menggunakan kaedah konvensional menghasilkan 0.47 mg/ml asid asetik. Selepas langkah hidrolisis enzim, pra-rawatan microwave telah menghasil gula yang lebih tinggi berbanding dengan kaedah pra-rawatan secara konvensional. Hasil kajian menunjukkan bahawa parameter pra-rawatan memainkan peranan penting dalam tren penghasilan glukosa dan xilosa daripada hidrolisis enzim SPB. Keputusan glukosa dan hasil xilosa dari pra-rawatan MSA dan hidrolisis enzim SPB telah dipilih untuk membangunkan model PSO–ANN hibrid. Model hibrid PSO–ANN menunjukkan pekali regresi (R^2) yang lebih tinggi bagi nilai anggaran dan eksperimen glukosa dan xilosa pada nilai 0.9939 dan 0.9479, masing-masing. Sementara itu, nilai R^2 model RSM hanya 0.8901 dan 0.8439 untuk glukosa dan xilosa, masing-masing.

Kajian ini menyimpulkan bahawa SPB mempunyai potensi untuk dibangunkan sebagai sumber gula untuk difermentasikan pada masa hadapan dan pra-rawatan berbantu gelombang mikro adalah satu laluan yang mungkin boleh digunaan untuk meningkatkan pembebasan gula ini.

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I certify that a Thesis Examination Committee has met on 23 February 2017 to conduct the final examination of Saleem Ethaib Mohammad on his thesis entitled "Microwave Assisted Pretreatment and Enzymatic Hydrolysis for Sugar Production from Sago Palm Bark" 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 Doctor of Philosophy.

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This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
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LIST OF ABBREVIATIONS

ADF	Acid Detergent Fibre
ADL	Acid Detergent Lignin
AFEX	Ammonia Fiber Explosion
ANN	Artificial Neural Network
ANOVA	Analysis of Variance
BBD	Box-Behnken Design
CAM	Cosine Amplitude Method
CI	Crystallinity Index
CSA	Conventional -Sulpheric Acid
CSB	Conventional -Sodium Bicarbonate
CSH	Conventional-Sodium Hydroxide
DNS	3,5-Dinitrosalicylic Acid Reagent
DOE	Design Of Experiment
DTG	Derivative Thermogravimetric Analysis
EDX	Energy Dispersive X-Ray Spectroscopy
ET	Exposure Time
FPA	Filter Paper Assay
FPU	Filter Paper Unit
GY	Glucose Yield
HMF	5-Hydroxymethylfurfural
HPLC	High-Performance Liquid Chromatography
IUPAC	International Union of Pure And Applied Chemistry
LHW	Liquid Hot Water

LM	Levenberg–Marquardt
LR	Learning Rate
MAE	Mean Squire Error
MAPE	Mean-Absolute Percent Error
MLP	Multi-Layer Perceptron
MP	Microwave Power
MSA	Microwave-Sulpheric Acid
MSB	Microwave-Sodium Bicarbonate
MSE	Mean Square Error
MSH	Microwave-Sodium Hydroxide
N	Number of Neurons in The Hidden Layer
NA	Not Available
ND	Not Detected
NDF	Neutral Detergent Fibre
NREL	National Renewable Energy Laboratory
OPF	Oil Palm Frond
OPT	Oil Palm Trunk
PSO	Particle Swarm Optimization
RMSE	Root-Mean-Squared Error
RSM	Response Surface Methodology
RST	Rice Straw
SE	Steam Explosion
SEM	Scanning Electron Microscopy
SE-MI	Steam Explosion And Microwave Irradiation
SL	Solid Loading

SPB	Sago Palm Bark
TGA	Thermogravimetric Analyser
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
XY	Xylose Yield

CHAPTER 1

INTRODUCTION

1.1 Background

Worldwide interest in the sustainable production of energy, fuel, pharmaceutical, and nutraceutical products has increased for many reasons in recent decades. There is an increasing demand for energy, food and materials due to global population growth and depleting reservoirs of raw fossil materials; global climate change and dramatic rises in food prices have caused worldwide concern about environmental issues and global food security. The use of renewable natural products such as lignocellulosic biomass as feedstock in the production of chemicals is considered a first step towards 'greening' the life cycle of chemical products. In recent years, efforts have focused on designing the products and processes of various industrial applications. These efforts attempt to minimize the use and generation of hazardous substances. Researchers focus on the use of technological approaches that utilize green chemical transformation into value-added derivatives. Thus, the minimal use of auxiliaries and minimal energy requirements e.g. diluted solvents and microwave heating applications will provide sustainable and feasible routes for the production of commodities specifically in biorefinery and nutraceutical industries.

Lignocellulosic biomass is the most abundant and widely available biopolymer on earth. Lignocellulosic biomass sourced from forestry, agricultural and agro-industrial residues has an estimated annual worldwide yield of 100-500 million dry tons, accounting for approximately half the total global biomass produced (Ibraheem and Ndimba, 2013). Therefore, it provides a unique and sustainable resource for sugar platform based chemicals and organic fuels because of its availability in enormous quantities at low cost, its richness in lignocellulose and its lack of competition with food crops (Sánchez and Cardona, 2008).

Sago palm (*Metroxylon sagu*) is one of the main commodity crops of Malaysia. The trunk of this tree is used as a raw material in the sago starch industry; however, more than 20,000 tons of the bark is discarded as a by-product per annum (Wahi et al., 2014). Therefore, a large quantity of stem residue, low-cost feed stock rich in lignocellulose could be recycled or reused for example, converted into useful products such as food, pharmaceutical products and other chemicals.

Lignocellulosic biomass comprises of three major components; cellulose, hemicellulose and lignin in addition to other minor components namely ash, pectin, protein and extractives. Both cellulose and hemicellulose comprise of polymeric sugars which create the potential to release fermentable sugars such as glucose and xylose during the hydrolysis stage which in turn, can be utilized in the manufacture of other products. Enzymatic hydrolysis is environmentally friendly because it takes place under mild processing conditions in comparison to acid or alkaline hydrolysis which requires further detoxification processes to remove the inhibitory effect of sugar by-products.

The enzymatic hydrolysis of lignocellulosic biomasses requires a pretreatment step due to the recalcitrance nature of cellulose, hemicellulose and lignin (Jorgensen et al., 2007). Hemicellulose fibers act like a glue that fills the voids between and around cellulose and hemicellulose fibers. The carbohydrate-rich cellulose and hemicellulose are covered by lignin on the outside, this preventing plant cell destruction, acting as a protective sheath against hydrolyzing enzymes (De Vries & Visser, 2001). The pretreatment of lignocellulose breaks down this recalcitrant by partially changing the matrix structure thereby enhancing accessibility to enzymes, releasing the corresponding monomers (fermentable sugars) from both cellulose and hemicellulose during the enzymatic hydrolysis step.

A pretreatment step is a key to the utilization of lignocellulosic materials and one of the most important and cost-prohibitive steps in the production of bio-alcohol compounds (Jorgensen et al., 2007). Various technologies, including physical and chemical pretreatment methods, have been developed for the pretreatment of lignocellulosic such as steam explosion (Öhgren et al., 2007), diluted acid (Kshirsagar et al., 2015), alkali (Zhang et al., 2011), hydrothermal pretreatments (Min et al., 2015) and ammonia fiber/freeze explosion (Moiser, 2005). Most of these pretreatment methods involve high processing costs due to harsh operational conditions e.g. high pressure and/or temperature. In addition, highly concentrated chemicals such as acids are toxic to the enzymes or the fermentative microorganisms, thus requiring an additional processing step. Since pretreatment is the first major unit of operation in the bioconversion process, it has a direct effect on the cost and efficiency of the steps which follow such as enzymatic hydrolysis and fermentation meaning that creating an effective pretreatment is extremely important. It should minimize the need to reduce the size of the biomass particles, preserve hemicellulose fractions, produce highly digestible pretreated substrates, lower or eliminate the generation of degradation products and inhibitory toxic substances and decrease energy requirements. Moreover, pretreatment agents such as solvents should be low cost and/or easily recycled (Alvira et al., 2010).

Microwave treatment of waste has gained more acceptance in recent years, thanks to the technological advances that make microwaving cheaper than it was 20 years ago. The main advantage of microwave heating is the small amount of time needed compared to conventional heating; minutes compared to hours. This is because of the fundamental difference between microwave and conventional heating in the heat transfer mechanism. Conventional heating requires surface heating first before the heat can be transferred inwards through conduction, convection or radiation. In microwave heating, the microwave energy interacts not only with the surface material but also penetrates the surface coming into contact with the core of the material at the same time (Muira et al., 2004). Therefore, microwave heating is a viable alternative to conventional heating methods having been widely applied in many fields because of its high heating rate and easy operation.

Microwave-assisted pretreatment utilizes both thermal and non-thermal effects generated by an extensive intermolecular collision as a consequence of the realignment of polar molecules such as water with microwave oscillations (Ma et al., 2009). Azuma et al. (1984) and Ooshima et al. (1984) reported that using microwaves for the pretreatment of lignocellulosic biomass has a positive effect on cellulosic material digestion for downstream processes such as rice straw. Recent studies on microwave-assisted pretreatment of different substrates have included wheat straw (Saha et al., 2008), rice straw (Zhu et al., 2006), corncob (Boonsombuti et al., 2013) and rice hull (Zhau et al., 2010). Although the operating factors of pretreatment such as microwave power (MP), exposure time (ET) and solid loading (SL) are varied between studies, the general perception is that microwave can disrupt the matrix structure of lignocellulose and enhance fermentable sugar release.

The utilization of 'green' solvents is encompassed by the overall goal to minimize the resulting environmental impact from the use of solvents in chemical production. A green and low energy pretreatment process can be achieved using microwave irradiation and low concentrates of solvents such as dilutions of sulfuric acid, sodium hydroxide and sodium bicarbonate. Using lower level of chemicals will make the pretreatment process more feasible and correspond with the general requirements for effective pretreatment (Jorgensen et al., 2007). Although the use of sodium hydroxide as a solvent has been examined by several research groups, there has been no study on sodium bicarbonate. Compared with other alkalis, sodium bicarbonate offers advantages such as low cost, safe handling and a high dielectric constant which might impact positively on microwave pretreatment via high heat generation at low power.

Response surface methodology (RSM) is a compilation of mathematical and statistical approaches commonly applied to the design of experiments (DOE) when building an empirical model for the experimental data obtained in relation to the experimental design. This method eliminates weaknesses associated with the classic one-variable-at-a-time strategy which fails to recognize the interactive effects of different variables on any measured response. Response surface experiments therefore attempt to identify the output or response of a system as a function of explanatory variables. This technique is capable of estimating the linear or square polynomial functions of input variables and the output response. Consequently, it is used to explore modeling and displacing experimental conditions until they are optimized (Betiku & Taiwo, 2015).

An artificial neural network (ANN) is one of the artificial intelligence techniques inspired by the structure and/or functional aspect of biological neural networks. Recently, ANN models have been employed to solve biotechnological problems related to the area of modeling and optimization to increase process efficiency; it can be applied as an alternative to polynomial regression-based model as it is suitable for modeling complex non-linear relationships (Armaghani et al., 2015). Although ANNs have the capacity to tackle complicated, nonlinear relationships between output responses and their affecting parameters, limitations do remain. For example, the optimal number of neurons in the hidden layer is not clear. It is determined by using a trial and error approach or randomly. This procedure may cause over fitting or under fitting problems for the ANN model. The number of neurons in hidden layers is critical. A higher number of neurons in a particular hidden layer can cause over fitting of the model where, instead of generalization of patterns in the training data set, the network memorizes the pattern. If the number of neurons is lesser, it leads to under fitting of model and hence more training time is needed to find optimum number of neurons (Hussain et al., 1992). Moreover, the optimum value of learning rate is not introduced and in fact often selected randomly causing slow performance in the intelligent system (Shi & Eberhart, 1998). Accordingly, the utilization of optimization algorithms such as particle swarm optimization (PSO) to solve ANN problems. It can determine the best number of neurons in the hidden layers, and select the optimum value of the learning rate of ANN, which in turn, can significantly improve ANN performance (Dezfouli et al., 2015; Gharghan et al., 2016). PSO algorithms represent a powerful iterative search algorithm that can be applied to solve ANN problems and increase performance. Recently, a number of researchers have confirmed the positive usage of hybrid PSO-ANN models to solve engineering issues such as estimating the ultimate bearing capacity of rock-socketed piles and to improve the accuracy of wireless sensor localization techniques (Gharghan et al., 2016; Armaghani et al., 2015). Therefore, a combination of these two artificial intelligent systems forming a hybrid PSO–ANN model can be used to improve estimations of the sugar yield for pretreatment and enzymatic hydrolysis of lignocellosic biomass.

1.2 Problem Statement

The utilization of lignocellulosic biomass as a raw material for fuel, food and pharmaceutical components industries is a global concern. Investigations include the development of feedstock alternatives using lignocellulosic biomass. Sago palms barks, a by-product generated by the sago starch industry, may constitute one of these alternatives implying that research into the characteristics and potential of SPB is essential.

Unfortunately, the complex structure of lignocellulosic materials makes it resistant to enzymatic hydrolysis. Therefore, the challenge is to produce a high sugar alcohol yield from lignocellulosic biomass in the hydrolysis stage using minimal amounts of energy and chemicals during pretreatment to reduce the investment cost. Current technologies including physical and chemical pretreatment methods result in relatively low sugar yields, severe reaction conditions and high processing costs. A neutralization process step is currently required as chemical solvents inhibit the enzymatic process during hydrolysis and fermentation steps (Chen et al., 2012a). A green and low energy pretreatment process is proposed using microwave irradiation to enhance enzyme susceptibility of lignocellolusic materials while the use of selective target heating reduces unnecessary waste. This study will investigate the use of low concentration solvents, their effect on fermentable sugar yield and the characteristics of the substrate. Very diluted solvents of sulfuric acid, sodium hydroxide and sodium bicarbonate will be employed to perform microwave-assisted pretreatments.

Response surface methodology (RSM) will be applied to the design of experiment (DOE) to build an empirical model for the experimental data obtained in relation to the experimental design in order to identify the interactive effects of different variables on any measured response.

An artificial neural network (ANN) will be applied as an alternative to polynomial regression-based model for modeling complex, non-linear relationships. Despite the fact of the ability of ANNs to render solutions for complicated and nonlinear relationship between output responses and its input parameters, limitations remain. Limitations such as the selection of the optimum values of the neurons in each hidden layer and the learning rate of ANN that play a significant role in optimization of estimating or forecasting results, are normally set based on either a trial and error procedure or at random. This can result in over fitting or under fitting problems for the model and slow performance of the intelligence system.

Consequently, particle swarm optimization (PSO) algorithms will be applied to determine the optimum values of the neurons in each hidden layer and the learning rate of ANN and thereby increase its performance. This study is believed to be the first study utilizing ANN coupled with PSO algorithms to estimate sugar yield for pretreatment and enzymatic hydrolysis of lignocellosic biomass.

1.3 Research Objectives

This study was carried out with the following objectives:

- To assess the effects of microwave-assisted pretreatment using diluted acid and alkaline solvents on sago palm bark characteristics and inhibitors formation.
- To evaluate the effects of microwave-assisted pretreatment parameters (operating conditions) on glucose and xylose yield via enzymatic hydrolysis.
- To develop an estimation model for glucose and xylose yield from the enzymatic hydrolysis of SPB based on microwave-assisted pretreatment conditions.

The process flow chart of this is study is shown in Figure 1 below:

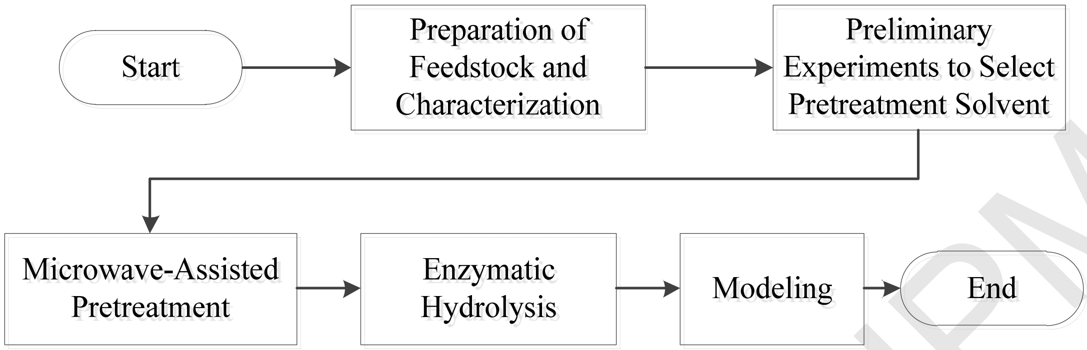

Figure 1.1 : The general research layout

1.4 Scope and Limitations

1. This research covers two of the major processes of conversion to sugar of lignocellulosic biomass, namely pretreatment and hydrolysis. The sample was taken through a primary microwave-assisted pretreatment, followed by an enzymatic hydrolysis process.
2. For the microwave-assisted pretreatment, three types of diluted chemicals are used as pretreatment solutions; sulphuric acid, sodium hydroxide and sodium bicarbonate at a range of concentrations of between 0.01 N and 0.1 N.
3. The pretreatment parameters (operating conditions) include solid loading, exposure time and microwave power.
4. Since there is no accurate procedure to directly measure the exact temperature and pressure of pretreatment in a domestic microwave oven, pretreatment was expressed in terms of the microwave power output that can be set on the instrument.
5. Sago palm bark was selected as the main source of lignocellulosic biomass in this study. Characterization of this material was carried out to identify the chemical components, this including elemental analysis, ash analysis, thermal properties, crystallinity analysis and morphology analysis.
6. Sugar analysis includes identifying the individual components for monomeric sugar using HPLC analysis according to the Renewable Energy Laboratory (NREL) procedure.
7. Inhibitors analysis was carried out to detect HMF (5-hydroxymethylfurfural), furfural and acetic acid only using HPLC analysis according to the NREL procedure. Formic acid is a degradation product of furfural and HMF, while levulinic acid is formed by the degradation of HMF (Ulbrich et al., 1984). As a result of the absence of HMF and furfural in the pretreatment liquor, analyses regarding formic acid and levulinic acid were not conducted.

1.5 Thesis Layout

This dissertation is organized into several chapters. Chapter 1 includes a general introduction. Chapter 2 offers a literature review with discussion focusing on lignocellulosic biomass as well as an overview of sago palm bark, including the pathways of conversion to platform sugars from lignocellulosic biomass. These processes include the pretreatment and hydrolysis steps and microwave fundamentals, as well as the microwave-assisted pretreatment overview and its governing parameters. Chapter 3 presents the impact of the microwave-assisted pretreatment method, using acid and alkali solvents, on sago palm bark characteristics and inhibitor formation. Chapter 4 reports the enzymatic hydrolysis for the pretreated materials using the microwave–assisted pretreatment and the effect of pretreatment parameters on sugar yields from sago palm bark via enzymatic hydrolysis using response surface methodology. The development of an estimation model for glucose and xylose yield from SPB microwave-assisted pretreatment via enzymatic hydrolysis using artificial intelligent systems is covered in Chapter 5. Finally, Chapter 6 summarizes the thesis with a conclusion and recommendations for future work.

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