DELIGNIFICATION OF PINEAPPLE PEEL WASTE BY SODIUM HYDROXIDE PRE-TREATMENT

VICKNESHWARAN KANNUCHAMI

A dissertation submitted in fulfilment of the
requirements for the award of degree of
Master of Engineering

School of Chemical and Energy Engineering
Faculty of Engineering
Universiti Teknologi Malaysia.

NOVEMBER 2018

To my lovely parent, who gave me endless love, trust, constant encouragement over the years and, for her prayers.

To my friends, for being very understanding and supportive in keeping me going, enduring ups and down during the completion of this thesis.

This dissertation is dedicated to them.

ACKNOWLEDGEMENT

I wish to express my deepest appreciation to all who have helped me, in one way or another, to complete this thesis. My sincerest gratitude to my supervisor Dr. Syed Anuar Faua'ad bin Syed Muhammad and Mr. Nik Azmi bin Nik Mahmood for their continuous guidance and support. With their expert guidance and immense knowledge, I was able to overcome all the obstacles that I have encountered during my journey to complete this thesis. I could not have imagined having a better advisor and mentor who has been more like a fatherly figure to me. Lastly, I graciously thank Mr. Ya'akob bin Sabudin from the Department of Bioprocess & Polymer Engineering for providing technical support.

ABSTRACT

Agriculture-based economies have caused the amount of lignocellulosic biomass wastes to be gradually increasing. It has been a major concern to all nations on the disposal method because it can cause major environmental problems. One of the largest agriculture residues contributing to this issue is pineapple waste. Pineapple waste especially the peels are the major by-product obtained during pineapple processing which contribute about 20 - 40 % of the total weight of the fruit. Since, pineapple peels rich in cellulose, it has huge potential use as substrate to develop into valuable bio-based materials. However, pre-treatment is required to overcome the complex structure of lignocellulosic biomass and make it accessible for enzymatic and microbial hydrolysis. In this study, chemical pre-treatment method was performed using alkaline solution, sodium hydroxide (NaOH) on pineapple peels waste. The first stage was the evaluation of the influence of NaOH concentration, temperature and retention time on degradation of lignin content using design of experiment, Box-Behnken and response surface methodology. Based from the Design-Expert software, the maximum lignin degradation was 55.5 % with the pre-treatment performed at 3 % NaOH concentration, 35.3 ^{o}C with 120 hr exposure time. The second stage of the study was evaluating the delignification kinetic. Kinetic data of the pre-treatment were evaluated at different temperatures (20 ^{o}C, 30 ^{o}C and 40 ^{o}C) at constant NaOH concentration, 3 % for 120 hr. Delignification by NaOH pre-treatment was possible at all levels of temperature in the bulk phase, however, results were more significant at temperatures 30 ^{o}C. The kinetic constant at 20 ^{o}C, 30 ^{o}C and 40 ^{o}C were 0.0093 h^{-1}, 0.1467 h^{-1} and 0.1649 h^{-1} respectively and the activation energy was 21.63 kJ/mol. The delignification was highly dependent on temperature and duration of pre-treatment.

ABSTRAK

Ekonomi berasaskan pertanian menyebabkan jumlah sisa biojisim lignoselulosik meningkat secara beransur-ansur. Ia menjadi kebimbangan utama kepada semua negara mengenai kaedah pelupusan sisa tersebut kerana ia boleh menyebabkan pencemaran kepada alam sekitar. Salah satu daripada residu pertanian terbesar yang menyumbang kepada isu ini ialah sisa nanas. Sisa nanas terutamanya kulit adalah produk sampingan utama yang diperoleh semasa pemprosesan pengeluaran nanas yang kira-kira 20 - 40 % daripada jumlah berat buah. Namun demikian, kulit nanas yang kaya dengan selulosa, hemiselulosa, gula dan karbohidrat lain menyebabkan ia mempunyai potensi besar yang boleh digunakan sebagai substrat untuk menghasilkan bahan yang berasaskan biologi yang lain. Walau bagaimanapun, pra-rawatan diperlukan untuk mengatasi struktur kompleks lignoselulosik tersebut supaya dapat dihidrolisis oleh enzim dan mikroorganism. Dalam kajian ini, kaedah pra-rawatan kimia digunakan iaitu natrium hidroksida (NaOH) pada sisa kulit nanas. Peringkat pertama adalah penilaian pengaruh kepekatan NaOH, suhu dan masa pengekalan terhadap penyingkiran lignin menggunakan reka bentuk uji kaji, *Box-Behnken and response surface methodology*. Penyingkiran lignin maksimum adalah 56.3 % dengan pra-rawatan dilakukan pada kepekatan NaOH 3 %, 30 ^{o}C dengan masa pendedahan 120 jam. Peringkat kedua kajian adalah *delignification kinetics*. Data kinetik pra-rawatan dinilai pada suhu yang berbeza (20 ^{o}C, 30 ^{o}C dan 40 ^{o}C) pada kepekatan NaOH tetap, 3 % selama 120 jam. Keputusan lebih ketara pada suhu 30 ^{o}C. Pemalar kinetik pada 20 ^{o}C, 30 ^{o}C dan 40 ^{o}C masing-masing 0.0093 h-1, 0.1467 h-1 dan 0.1649 h-1 dan tenaga pengaktifan yang diperlukan untuk memulakan tindak balas adalah 21.63 kJ / mol. Proses delignifikasi sangat dipengaruhi oleh sushu and masa pengekalan.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE

CHAPTER	TITLE	PAGE

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

H_2SO_4	-	Sulphuric acid
NaOH	-	Sodium hydroxide
Hr	-	Hours
Min	-	Minute
CO	-	Carbon monoxide
CO_2	-	Carbon dioxide
H_2	-	Hydrogen
SO_2	-	Sulphur dioxide
ClO_2	-	Chlorine dioxide
NO_2	-	Nitrogen dioxide
H_2O_2	-	Hydrogen peroxide
NH_3	-	Ammonia
$(NH_4)_2SO_3$	-	Ammonium sulphite
HCl	-	Hydrochloric acid
H_3PO_4	-	Phosphoric acid
O_3	-	Ozone
CH_3COOH	-	Acetic acid
KOH	-	Potassium hydroxide
$Ca(OH)_2$	-	Calcium hydroxide
$NH_3 \cdot H_2O$	-	Aqueous ammonia
$C_4H_4O_4$	-	Maleic or fumaric acid
$C_2H_2O_4$	-	Oxalic acid
HMF	-	hydroxymethylfurfural
MPIB	-	Malaysian Pineapple Industry Board
TAPPI	-	Technical Association of Pulp and Institute’s
AFEX	-	Steam explosion, ammonia fibre explosion

LIST OF ABBREVIATIONS

RSM	-	Response Surface Methodogy.
ml	-	Mililitre
g	-	Gram
w/v	-	Weight over volume
%	-	Percentage
^{o}C	-	Degree celcius
s	-	Seconds

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Lignocelluloses biomass is the most promising feedstock as it produces naturally, inexpensive, abundant and renewable resources. The biomass is mainly consisting three components such as cellulose, hemicelluloses and lignin. Cellulose consists of long chained glucose subunits that linked together by 1, 4-glycosidic bonds (Lee, Hamid, & Zain, 2014). Hemicellulose is polymers consist of glucose units which contain different type of sugars. But, sugar units in hemicellulose are smaller and branched polymers compare to cellulose. Lignin is a more complex polymer compare to other components in biomass. The polymers cross linked chains that formed with phenylpropane units serves as a protective layer. All the three components are covalent cross-linkages that make biomass a complex composite material (Amin *et al*., 2017).

Pineapple (*Ananas comosus*) wastes are one of the largest amount lignocellulosic feedstock waste produced throughout the world (Hajar *et al*., 2012; Tropea *et al*., 2014). The worldwide production of pineapple is 16 million tons in 2005 and is exported in its fresh or processed form such as canned pineapple,

pineapple pulp and juice. Among the leading producer of pineapple are China, India, Thailand, Brazil, Colombia, Kenya and Nigeria. In Malaysia, pineapple industry is relatively small compared to other agro-based export oriented industry such as palm oil and rubber, however it play an important role in developing the country's socio-economic (Ong, Tan, & Liew, 2014). In Malaysia, 412, 720 metric tons of pineapple based products was produced in 2015 and currently world's 18th largest pineapple producer. By the year of 2020, the intensification of Malaysia's pineapple plantation parallel with 11th Malaysia Plan is forecasted to contribute in larger pineapple production among other leading producer of pineapple (Ruekeith, 2015).

Pineapple peels which are rich in intracellular sugars have great potential to be converted into different valuable products such as bio-fuels, bio-energy, fine chemicals, energy source for microbial fermentation and enzyme production (Anwar, Gulfraz, & Irshad, 2014; Tropea *et al*., 2014). However, the pineapple peels has limitation for utilization due to cellulose, hemicelluloses and lignin are tightly associated with each other and makes the biomass less accessible for microorganisms or enzyme digestion. Therefore, pre-treatment is an important tool in order to break down the structure for better enzyme accessibility before the raw material can be used for bioconversion to produce value added products. During pre-treatment process, the compact structure of the biomass will be disrupted by breaking down the lignin structure, decreases the crystallinity of cellulose and degrade hemicelluloses to sugar monomers. Eventually, it makes cellulose fibre more exposed for the enzymes and microorganism to access and hydrolyses the cellulose to convert the carbohydrate polymers into fermentable sugars (Amin *et al*., 2017).

There are several methods of pre-treatment that were used to the disrupt complex structure of lignocellulosic biomass such as mechanical, physicochemical, chemical and biological pre-treatments. Among the various treatment methods, chemical pre-treatment using alkaline solution pre-treatment is widely studied. Alkaline pre-treatment using sodium hydroxide, NaOH is proven as cost effective, less amount of energy amd non-hazardous chemical process. The major advantage of NaOH pre-treatment is efficient breakdown of lignin from the biomass without any momentous loss of structural carbohydarate materials such as glucose, xylose, arabinose and so on from different types of lignocellulosic biomass like sugarcane bagasse, switch grass and corn stover from previous studies (Amin *et al*., 2017; Chen, Stevens, Zhu, Holmes & Xu, 2013; Kumar, Barrett, Delwiche & Stroeve, 2009). Therefore, NaOH pretreatment is a promising pre-treatment option for both types of woody and non-woody types of lignocellulosic biomass. In this study, pineapple peels waste was used as the biomass to determine the influence of NaOH concentration, temperature and retention time in lignin removal using Response Surface Methodology (RSM) and delignification kinetics.

1.2 Problem Statement

The worldwide production of lignocellulosic biomass waste is estimated about 1.3×10^{10} metric tons per annum. It is predicted that biomass generation to be increasing annually. Pineapple wastes which comprise about 2000 species are one of the major contributors for the increase in lignocellulosic wastes globally which produces annually over 14 million tons worldwide. It is the eighth most abundantly produced fruit in the world (Amin *et al*., 2017; Hajar *et al*., 2012). In Malaysia, it is forecasted that the amount of pineapple waste will significantly increase as a consequence of intensified pineapple plantation and canned fruit production in the country by the year of 2020 (Ruekeith, 2015). During pineapple processing, almost 50% of total fruit weight is removed as waste such as stem, crown, peel and core. Therefore, pineapple wastes are proportionally increasing with the increase in pineapple production (Saravanan, Muthuvelayudham, & Vruthagiri, 2013). It causes serious environmental problems since only fewer amount of the pineapple waste are crushed and used as animal feed but most of them are dumped into the environment which causes anaerobic digestion due to microbial spoilage (Ong, Tan, & Liew, 2014).

As a result, formation of methane gas occurs in the absence of oxygen condition causes major environmental problems such as global warming. In addition, dumping pineapple waste in soil also cause groundwater pollution and land degradation (Chulalaksananukul, Sinbuathong & Chulalaksananukul, 2012). Therefore, the interest in research in pineapple wastes utilization to produce valuable bio-sourced materials have increased such as production of biofuels, biogas, fine chemicals, energy source and enzyme production (Anwar, Gulfraz & Irshad, 2014). Pineapple waste has great potential to be used as raw material for reprocessing that will benefit the environment and economy (Itelina *et al*., 2013; Saravanan, Muthuvelayudham, & Vruthagiri, 2013).

However, developments of the pineapple wastes conversion to valuable products still remain a big challenge. It has evolved to resist degradation as physicochemical structural and compositional factor such as thick layer of lignin makes them resistant to enzymatic and chemical degradation. It hinders the breakdown of cellulose in pineapple wastes to sugar units or other organic compounds. Therefore, pre-treatment processes are important to be applied in order to remove lignin and reduce hemicelluloses to sugar monomers as it break down bonds linked in the complex chains of biomass (Amin *et al*., 2017; Kumar, Barrett, Delwiche & Stroeve, 2009).

Furthermore, it also removes inhibitors and decreases the crystalline structure. This enables the enzymes and microorganisms access easily into the structure and digests the cellulose chains. Moreover, pre-treatment is also important in producing value added products at high selectivity and yields at economical costs. Among the various pre-treatment techniques, alkaline pre-treatment shows highest improvement in lignocellulosic breakdown rates by altering the physical and chemical structure. Previous studies show that the following pre-treatment have improved the yields above 90% from the theoretical yield for lignocellulosic biomasses such as grasses, corn, rice husk and others (Amin *et al*., 2017; Kumar, Barrett, Delwiche & Stroeve, 2009).

1.3 Objectives

i. To identify the degradation of lignin content in pineapple peels waste after NaOH pre-treatment.

ii. To study the delignification kinetic and determine its activation energy.

1.4 Scope of Study

The following scopes are performed to acquire the objectives:

i. Identify the degradation of lignin content in pineapple peels waste after pre-treated with NaOH at different concentration range, temperature and retention time using RSM.

ii. Evaluate delignification kinetic and determine activation energy of pineapple peels waste after the pre-treatment using Arrhenius equation.

1.5 Significance of Study

The research study will aid to attain maximum degradation of lignin content from pineapple peels waste after pre-treatment with NaOH at different parameter of NaOH concentration, temperature and retention time. Furthermore, the study aid to determine the amount of energy required for pineapple peels waste to initiate the reaction after pre-treatment.

1.6 Thesis Organization

This thesis consists of 5 chapters which represents the sequence works of this research.

Chapter 1 describes the overview of lignin degradation in pineapple peels waste after pre-treatment with NaOH including background of study, problem statement, objective, scope and significance of the study.

Chapter 2 consists of the general and scientific information about lignocellulosic physical and chemical properties, potential of agricultural wastes to produce bio-based products, potential and characteristics of pineapple waste, pre-treatment of lignocellulosic biomass and delignification of pineapple peels wastes.

Chapter 3 describes the methodology involving characterization of pineapple peels waste, experimental procedure of pineapple peels wastes with NaOH and alkaline delignification to determine the activation energy using Arrhenius equation.

Chapter 4 covers the results obtained from the study by the experimental parameter tested and kinetic of pineapple peels waste delignification using Arrhenius equation.

Finally, chapter 5 covers the conclusion of the study. In this chapter, final conclusion on the optimum condition of lignin degradation in pineapple peels waste after pre-treatment with NaOH and its activation energy are identified.

1.7 Summary

Increasing of lignocellulosic biomass waste has made a major concern to all nations on the disposal method as it causes major environmental problems. One of the largest agriculture residues contributing to this matter is pineapple waste. Since pineapple peels rich in cellulose, hemicelluloses, sugars and other carbohydrates, it has huge potential use as substrate to be developed into valuable bio-based materials. However, pre-treatment methods are essential in order to overcome the complex structure of lignocellulosic biomass by making them accessible for enzymatic and microbial hydrolysis. Therefore, chemical pre-treatment, sodium hydroxide solution was used in order to degrade the lignin content in the pineapple peels waste. The influences of several parameters such as NaOH concentration, temperature and retention time on degradation of lignin were optimized and its activation energy is determined.

REFERENCES

Abdullah, & Mat, H. (2008). Characterization of Solid and Liquid Pineapple Waste. *Reactor, 12*, 48-52.

Achinas, S., & Euverink, G. J. W. (2016). Consolidated Briefing of Biochemical Ethanol Production from Lignocellulosic Biomass. *Electronic Journal of Biotechnology*. *23,* 44-53.

Amin, F. R., Khalid, H., Zhang, H., Rahman, S. U., Zhang, R., Liu, G., & Chen, C. (2017). Pretreatment Methods of Lignocellulosic Biomass for Anaerobic Digestion. *AMB Express*, *7*(72). 1-12.

Anwar, Z., Gulfraz, M., & Irshad, M. (2014). Agro-industrial Lignocellulosic Biomass a Key to Unlock the Future Bio-energy: A Brief Review. *Journal of Radiation Research and Sciences*, *7*, 163-173.

Ayeni, A. O., Omoleye, J. A., Hymore, K. F., & Pandey, A. A. (2016). Effective Alkaline Peroxide Oxidation Pre-Treatmentoh Shea Tree Sawdust for the Production of Biofuel: Kinetics of Delignification and Enzymatic Conversion to Sugar and Sunsequent Production of Ethanol by Fermentation using *Saccharomyces cerevisiae*. *Brazilian Journal of Chemical Engineering*. *33*(1), 33-45.

Balan, V. (2014). Current Challenges in Commercially Producing Biofuels from Lignocellulosic Biomass. *ISRN Biotechnology*, 1-31.

Bardiya, N., Somayaji, D., & Khanna, S. (1996). Biomethanation of Banana Peel and Pineapple Waste. *Bioresource Technology*, *58*(1), 73-76.

Bas, D., & Boyacı, İ. H., (2007). Modeling and optimization: Usability of response surface methodology. *Journal of Food Engineering*, *78*(3), 836–845.

Bensah, E. C., & Mensah, M. (2013). Chemical Pretreatment Methods for the Production of Cellulosic Ethanol: Technologies and Innovations. *International Journal of Chemical Engineering*, *11*, 1-21.

Bezerra, M. A., Santelli, R. E., Oliveira, E. P., Villar, L. S., & Escaleira, L. A. (2008). Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta*, *76*(5), 965–977.

Bhagwat, S., Ratnaparkhe, S., & Kumar, A. (2015). Biomass Pre-treatment Methods and Their Economic Viability for Efficient Production of Biofuel. *British Biotechnology Journal*, *8*(2), 1-17.

Brodeur, G., Yau, E., Badal, K., Collier, J., Ramachandran, K. B., & Ramakrishnan, S. (2011). Chemical and Physiochemical Pretreatment of Lignocellulosic Biomass: A Review. *Enzyme Research*, 1-17.

Cesaro, A., & Belgiorno, V. (2015). Combined Biogas and Bioethanol Production: Opportunities and Challenges for Industrial Application. *Energies*, *8*, 8121-8144.

Chen, S., Zhang, X., Singh, D., Yu, H., & Yang, X. (2014). Biological Pre-treatment of Lignocellulosics: Potential, Progress and Challenges. Journal of Biofuel, *1*(1), 177-199.

Chen, Y., Stevens, M. A., Zhu, Y., Holmes, J., & Xu, H. (2013). Understanding of Alkaline Pretreatment Parameters for Corn Stover Enzymatic Saccharification. *Biotechnology for Biofuels*, *6*(8), 1-10.

Chen, Y., Sharma-Shivappa, R. R., Keshwani, D., Chen, C., 2007. Potential of Agricultural Residues and Hay for Bioethanol Production. Applied . Biotechnology. *142*(3), 276-290.

Choonut, A., Saejong, M., & Sangkharak, K. (2014). The Production of Ethanol and Hydrogen from Pineapple Peel by *Saccharomyces cerevisiae* and *Enterobacter aerogenes*. *Energy Procedia*, *52*, 242-249.

Chulalaksananukul, S., Sinbuathong, N., & Chulalaksananukul, W. (2012). Bioconversion of Pineapple Solid Waste under Anaerobic Condition through Biogas Production. *KKU Research Journal*, *17*(5), 734-742.

Cotana, F., Barbanera, M., Foschini, D., Lascaro, E., & Buratti, C. (2015). Preliminary Optimization of Alkaline Pretreatment for Ethanol Production from Vineyard Pruning. *Energy Procedia*, *82*, 389-394.

Dang, V. O. & Nguyen, K. L. (2008). A Universal Kinetic model for Charaterzation of the effect of chip thickness on kraft pulping. *Bioresource Technology, 99,* 1586-1490.

Deressa, L., Libsu, S., Chavan, R. B., Manaye D., & Dabassa, A. (2015). Production of Biogas from Fruit and Vegetable Wastes Mixed with Different Wastes. *Environmental and Ecology Research*, *3*(3), 65-71.

Dussan, K. J., Silva, D. D. V., Moraes, E. J. C., Arruda, P. V., & Felipe, M. G. A. (2014). Dilute-acid Hydrolysis of Cellulose to Glucose from Sugarcane Bagasse. *The Italian Association of Chemical Engineering*, *38,* 433-438.

Eisenhuber, K., Krennhuber, K., Steinmuller, V., & Jager, A. (2013). Comparison of Different Pre-treatment Methods for Separating Hemicelluloses from Straw During Lignocelluloses Bioethanol Production. *Energy Procedia*, *40*, 172-181.

El-Tayeb, T. S., Abdelhafez, A. A., Ali, S. H., & Ramadan, E. M. (2012). Effect of Acid Hydrolysis and Fungal Bio-treatment on Agro-industrial Wastes for Obtainment of Free Sugars for Bioethanol Production. *Brazilian Journal of Microbiology, 43*(4), 1523-1535.

Ferreira, S. L. C., Bruns, R. E., Ferreira, H. S., Matos, G. D., David, J. M., Brandao, G. C., Silva, E. G. P., Portugal, L. A., Reis, P. S., Souza, A. S., & Santos, W. N. L. (2007). Box-Behnken Design: An Alternative for the Optimization of Analytical Methods. *Analytica Chimica Acta*, *507,* 179-186.

Fujii, T., Fang, X., Inoue, H., Murakami, K., & Sawayama, S. (2009) Enzymatic hydrolyzing performance of *Acremonium cellulolyticus* and *Trichoderma reesei* against three lignocellulosic materials. *Biotechnology and Biofuels*, *2*(24), 1-8.

Fuentes, L. L. G., Rabelo, S. C., Filho, R. M., & Costa, A. C. (2011). Kinetics of Lime Pretreatment of Sugarcane Bagasse to Enchance Enzymatic Hydrolysis. *Applied Biochemistry Biotechnology*, *163,* 612-625.

Ghorbani, F., Karimi, M., Biria, D., Kariminia, H., R. & Jeihanipour, A. (2015). Enhancement of Fungal Delignification of Rice Straw by *Trichoderma viride sp*. to Improve its Saccharification. *Biochemical Engineering Journal*. *101*, 77-84.

Grimaldi, M. P., Marques, M. P., Laluce, C., Cilli, E. M. & Sponchiado, S. R. P. (2015). Evaluation of Lime and Hydrothermal Pretreatments for Efficient Enzymatic Hydrolysis of Raw Sugarcane Bagasse. *Biotechnology for Biofuels*, *8*(205), 1-14.

Guilherme, A. A., Dantas, P. V. F., Santos, E. S., Fernandes, F. A. N. & Macedo, G. R. (2015). Evaluation of Composition, Characterization and Enzymatic Hydrolysis of Pre-treated Sugar Cane Bagasse. *Brazilian Journal of Chemical Engineering*, *32*(1), 23-33.

Hajar, N., Zainal, S., Nadzirah, K. Z., Roha, S. A. M., Atikah, O., & Elida, T. Z. M. (2012). Physicochemical Properties Analysis of Three Indexes Pineapple (*Ananas Comosus)* Peel Extract Variety N36. *APCBEE Procedia*, *4*, 115-121.

Hamzah, N. H. C., Markon, M., Harun, S., & Hassan, O. (2016). The Effect of Various Pretreatment Methods on Empty Fruit Bunch for Glucose Production, *Malaysian Journal of Analytical Sciences*, *20*(6), 1474-1480.

Harmsen, P. F. H., Huijgen, W. J. J., Lopez, L. M. B., & Bakker, R. R. C. (2010). Literature Review of Physical and Chemical Pretreatment Processes for Lignocellulosic Biomass. *Food and Biobased Research*, 1-49.

Iberahim, N. I., Jahi, J. M., Harun, S., Nor, M. T. M., & Hassan, O. (2013). Sodium Hydroxide Pretreatment and Enzymatic Hydrolysis of Oil Palm Mesocarp Fiber. *International Journal of Chemical Engineering and Applications*, *4*(3), 101-105.

Ioelovich, M. & Morag, E. (2012). Study of Enzymatic Hydrolysis of Mild Pretreated Lignocellulosic Biomasses. *BioResources*, *7*(1), 1040-1052.

Isikgor, F. H., & Becer, C. R. (2015). Lignocellulosic Biomass: A Sustainable Platform for the Production of Bio-based Chemicals and Polymers. *Polymer Chemistry*, *6*, 4497-4559.

Islam, M. S., Kao, N., Bhattacharya, S. N., & Guota, R. (2017). Optimization and Modelling of Delignification Process for Nanocrystalline Cellulose Production from Rice Husk Biomass. *AIP Conference Proceedings 1914, 030005*, 1-7.

Itelina, J., Onwuliri, F., Onwuliri, E., Onyimba, I., & Oforji, S. (2013). Bio-ethanol Production from Banana, Plantain and Pineapple Peels by Simultaneous Saccharification and Fermentation Process. *International Journal of Environmental Science and Development*, *4*(2), 213-216.

Jonsson, L. J., & Martin, C. (2016). Pretreatment of Lignocellulose: Formation of Inhibitory By-products and Strategies for Minimizing Their Effects. *Bioresource Technology*, *199*, 103-112.

Jung, W., Savithri, D., Shivappa, R. S., & Kolar, P. (2018). Article Changes in Lignin Chemistry of Switchgrass due to Delignification by Sodium Hydroxide Pretreatment. *Energies*, *11*(376), 1-12.

Kamm B., & Kamm M. (2004). Principles of biorefineries. *Applied Microbiology and Biotechnology*, 64, 137-145.

Kamm B., Kamm M., Gruber P., R., & Kromu S. (2006). Biorefinery systems – An overview, Biorefineries-Industrial process and products. Vol. 1, Kamm B., Gruber P., R., Kamm M., Eds., Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, pp.3-40.

Kandasamy, M., Hamawand, I., Bowtell, L., Seneweera, S., Chakrabarty, S., Yusaf, T., Shakoor, Z., Algayyim, S., & Eberhard, F. (2017). Investigation of Ethanol Production Potential from Lignocellulosic Material Without Enzymatic Hydrolysis Using the Ultrasonic Technique. *Energies*, *10*(62), 1-12.

Kang, N., Liu, Z., Hui, L. F., Si, C. L., Cui, L., Zhao, T., & Mao, S. T. (2012). Study on the Optimum Process of Acid-Catalytic Ethanol Pre-treatment of Chinese Triploid Poplar to Enhance Sugar Recovery by Hydrolysis. *Bioresources*, *7*(1), 578-592.

Karimi, K., & Taherzahed, M. J. (2016). A Critical Review of Analytical Methods in Pretreatment of Lignocellllluloses: Composition, Imaging and Crystallinity. *Bioresource Technology*, *200*, 1008-1018.

Kataria, R. & Ghosh, S. (2014). NaOH Pretreatment and Enzymatic Hydrolysis of *Saccharum spontaneum* for Reducing Sugars Production. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, *36*(9), 1028-1035.

Ketnawa, S., Chaiwut, P., & Rawdkuen, S. (2012). Food and Bioproducts Processing Pineapple Wastes: A Potential Source for Bromelain Extraction. *Food and Bioproducts Processing*, *90*(3), 385–391.

Kim, B., Gulati, I., Park, J. & Shin, J. D. (2012). Pretreatment of Cellulosic Waste Sawdust into Reducing Sugars using Mercerization and Etherification. *BioResources*. 7(*4)*, 5152-5166.

Kristiana, A., Effendib, N., Ariatiawana, Y., Auliaa, F., & Sudiyani, Y. (2015). Effect of Combining Chemical and Irradiation Pre-treatment Process to Characteristic of Oil Palm's Empty Fruit Bunches as Raw Material for Second Generation Bioethanol. *Energy Procedia*, *68*, 195-204.

Kumar, P., Barrett, D. M., Delwiche, M. J., & Stroeve, P. (2009). Methods for Pretreatment of Lignocellulosic Biomass for Efficient Hydrolysis and Biofuel Production. *Indian Engineering Chemical Resources*, *48*(8), 3713-3729.

Koradiya, M., Duggirala, S., Tipre, D., & Dave, S. (2016). Pre-treatment Optimization of Sorghum Pioneer Biomass for Ethanol Production and its Scale-ups. *Bioresource Technology*, *199*, 142-147.

Lee, H. V., Hamid, S. B. A., & Zain, S. K. (2014). Conversion of Lignocellulosic Biomass to Nanocellulose: Structure and Chemical Process. *The Scientific World Journal*, 1-20.

Lenihan P., Orozco A., O'Neill E., Ahmad M. N. M., Rooney W., & Walker G. M. (2010), Dilute Acid Hydrolysis of Lignocellulosic Biomass. *Chemical Engineering Journal*. 156(*2*), 395-403.

Liyana-Pathirana, C., & Shahidi, F. (2005). Optimization of Extraction of Phenolic Compounds from Wheat using Response Surface Methodology. *Food Chemistry*, *93*(1), 47–56.

Loow, Y. L., Wu, T. Y., Yang, G. H., Md. Jahim, J., Teoh, W. H., & Mohammad, A. W. (2016). Role of energy irradiation in aiding pretreatment of lignocellulosic biomass for improving reducing sugar recovery. *Cellulose*, *23*(5), 2761-2789.

Maurya, D. M., Singla, A., & Negi, S. (2015). An Overview of Key Pretreatment Processes for Biological Conversion of Lignocellulosic Biomass to Bioethanol. *Biotechnology Journal*, *5*, 597-609.

Mulyono, N., Rosmelia, E., Moi, J. G. P., Valentine, B. O., & Suhartono, M. T. (2013).Quantity and Quality of Bromelain in Some Indonesian Pineapple Fruits. *International Journal of Applied Biology and Pharmaceutical Technology*, *4*(2), 235-240.

Musa, Z. (2014, March 31). Demand for pineapples. Retrieved From the Star Online website: http://www.thestar.com.my/news/community/2014/03/31 Demand-for-pineapples-three-new markets-show-interest-in-the-fresh-fruit

Mourabet, M., Rhilassi, A. E., Boujaady, H. E., Ziatni, M. B., & Taitai, A., (2017). Use of Response Surface Methodology for Optimization of Fluoride Adsorption in an Aqueous Solution by Brushite. *Arabian Journal of Chemistry*. *10*, 3292-2202.

Nadzirah, Zainal, K. Z., Noriham, S., Normah, A., Roha, S., Nadya, H. (2013). Physico-chemical Properties of Pineapple Variety N36 Harvested and Stored at Different Maturity Stages. *International Food Research Journal*, *20*(1), 225-231.

National Renewable Energy Laboratory (NREL) (2017, June 10). Biorefinery. Retrieved From the NREL website : http://www.nrel.gov/biomass/biorefinery.html.

Nguyen, Q. A., Tucker, M. P., Keller, F., A. & Eddy, F. P. (2000). Two-stage Dilute-acid Pre-treatment of Softwoods. *Applied Biochemical Biotechnology*, *84*(86), 561-576.

Ong, K. L., Tan, B. W., & Liew, S. L. (2014). Pineapple Cannery Waste as a Potential Substrate for Microbial Biotransformation to Produce Vanillic Acid and Vanillin. *International Food Research Journal*, *21*(3), 953-958.

Orozco, R. S., Hernandez, P. B., Morales, G. B., Nunez, F. U., Villafuerta, J. O., Lugo, V. L., Ramirez, N. F., Diaz, C. E. B., & Vazquez, P. C. (2014). Charaterization of Lignocellulosic Fruits Waste as an Alternative Feedstock for Bioethanol Production. *BioResources*, *9*(2), 1873-1885.

Pardo-Rueda, A. J., Quintero-Ramos, A., Genovese, D. B., Camacho-Davila, A., Zepeda-Rodríguez, A., Contreras-Esquivel, J. C., & Bizarro, A. P. (2015). Efficient Extraction of Fructans from Sotol Plant (Dasylirion leiophyllum) Enhanced by a Combination of Enzymatic and Sonothermal Treatments. *Food and Bioproducts Processing*, 94, 398-404.

Pedersen, M., Johansen, K. S. & Meyer, A. S. (2011). Low Temperature Lignocellulose Pre-treatment: Effects and Interactions of Pre-treatment pH are critical for maximizing enzymatic monosaccharide yields from wheat straw. *Biotechnology Biofuels*, *4*(11), 1-10.

Pei, P., Zhang, C., Li, J., Chang, S., Li, S., Wang, J., Zhao, M., Jiang, L., Yu, M., & Chen, X. (2014). Optimization of NaOH Pretreatment for Enhancement of Biogas Production of Banana Pseudo-Stem Fiber Using Response Surface Methodology. *BioResources*, *9*(3), 5073-5087.

Penjumras, P., Rahman, R. A., Talib, R. A. & Abdan, K. (2015). Response Surface Methodology for the Optimization of Preparation of Biocomposites Based on Poly(lactic acid) and Durian Peel Cellulose. *The Scientific World Journal*, 1-12.

Pothiraj, C., Kanmani, P., & Balaji, P. (2006). Bioconversion of Lignocelluloses Materials. *Mycobiology*, *34*(4), 159-165.

Rocha G. J. M., Martin C., Silva V. F. N., Gomez E. O., & Golcalves A. R. (2012). Mass Balance of Pilot-Scale Pretreatment of Sugarcane Bagasse by Steam Explosion Followed by Alkaline Delignification. *Bioresource Technology*, *111*, 447-452.

Roha, S., Zainal, A. M., Noriham, S., & Nadzirah, K. Z. (2013). Determination of Sugar Content in Pineapple Waste Variety N36. *International Food Research Journal*, *20*(4), 1941-1943.

Ruekeith, G. O. (2015). Malaysia Pineapple Industry Board Looks to Control Five Per Cent of The Global Market. (2015, November 30). Retrieved From the Borneo Post Online website: http://www.theborneopost.com/2015/11/30/malaysia-pineapple-industry-board-looks-to-control-five-per-cent-of-the-global-market

Saravanan, P., Muthuvelayudham, R., & Vruthagiri, T. (2013). Enhanced Production of Cellulose from Pineapple Waste by Response Surface Methodology. *Journal of Engineering*, *4*, 1-8.

Sasmal, S., Goud, V. V., & Mohanty, K. (2013). Delignification Kinetics of Lime Pretreatment – An Ineluctable Tread for Augmenting Saccharification. *Journal of Biobased Materials and Bioenergy*, *7*(5), 660-664.

Singh, D. P., & Trivedi, R. K. (2013). Acid and Alkaline Pretreatment of Lignocellulosic Biomass to Produce Ethanol as Biofuel. *International Journal of Chemical Technology Research*, *5*(2), 727-734.

Sjostrom, E., 1993. Wood Chemistry: Fundamentals and Applications, second ed. Academic Press, Orlando.

Soontornchaiboon, W., Kim, S. M., & Pawongrat, R. (2016). Effects of Alkaline Combined with Ultrasonic Pretreatment and Enzymatic Hdyrolysis of Agricultural Wastes for High Reducing Sugar Production, *Sains Malaysiana*, *45*(6), 955-962.

Soumya, P. S., Lakshmi, M. S. K. & Nambisan, P. (2016). Application of Response Surface Methodology for the Optimization of Laccase Production from *Pleurotus ostreatus* by Solid State Fermentation on Pineapple leaf Substrate. *Journal of Scientific & Industrial Research*, *75*, 306-314.

Sun, Y. & Cheng, J. (2002). Hydrolysis of Lignocellulosic Materials for Ethanol Production: A Review. *Bioresource Technology*, *83*(1), 1-11.

Taherzahed, M. J., Karimi, K. (2008). Pretreatment of Lignocelllulosic Waste to Improve Ethanol and Biogas Production: A Review. *International Journal of Molecular Sciences*, *9*, 1621-1651.

Taniguchi, M., Suzuki, H., Watanabe, D., Sakai, K., Hoshino, K., & Tanaka, T. (2006). Evaluation of Pre-treatment with Pleurotus Ostreatus for Enzymatic Hydrolysis of Rice Straw. *Journal of Bioscience and Bioengineering*, *100*(6), 637-643.

Tropea, A., Wilson, D., Torre, L. G., Curto, R. B., Saugman, P., Davies, P. T., Dugo G., & Waldron, K. W. (2014). Bioethanol Production from Pineapple Wastes. *Journal of Food Research*, *3*(4), 60-70.

Tutt, M., Kikas, T., & Olt, J. (2012). Influence of Different Pretreatment Methods on Bioethanol Production from Wheat Straw. *Agronomy Research*, *1*, 269-276.

Upadhyay, A., Lama, J. P., & Tawata, S. (2010). Utilization of Pineapple Waste: A Review. *Journal of Food Science and Technology Nepal*, *6*, 10-18.

Viswanath, P., Devi S. S., & Nand K. (1992). Anaerobic Digestion of Fruit and Vegetable Processing Waste for Biogas Production. *Bioresource Technology*, *40*(1), 43-48.

Wang, Z., Li, J., Barford, J. P., Hellgradt, K. & McKay, G. (2016). A Comparison of Chemical Treatment Methods for the Preparation of Rice Husk Cellulosic Fibers. *International Journal of Environmental & Agriculture Research*, *2*(1), 67-77.

Wi, S. G., Cho, E. J., Lee, D. S., Lee, S. J., Lee, Y. J., & Bae, H. J. (2015). Lignocellulose Conversion for Biofuel: New Pretreatment Greatly Improves Downstream Biocatalytic Hydrolysis of Various Lignocellulosic Materials. *Biotechnology for Biofuels*, *8*(228), 2-11.

Wyman, C. E., (2008). Cellulosic Ethanol: A Unique Sustainable Liquid Transportation Fuel. *Resources: Biomass & Biofuels*, *33*, 381 - 383.

Yingkamheng, N., & Sukyai, P. (2014) The Potential of Mango Peel Utilization for Cellulose Extraction by Hydrothermal Pretreatment. *Thai Society for Biotechnology and International Conference*. 101-109.

Zabihi, S., Alinia, R., Esmaeilzadeh, F., & Kalajahi, J. F. (2010). Pretreatment of wheat straw using steam, steam/acetic acid and steam/ethanol and its enzymatic hdyrolysi for sugar production. *Biosystem Engineering*. *105*(3), 288-297.

Zeikus, J., G., Jain, M., K., & Elankovan, P. (1999) Biotechnology of Succinic Acid Production and Markets for Derived Industrial Product. *Applied Microbiology and Biotechnology*. *51*(5), 545-552.

Zhao, Y., Wang, Y., Zhu, J., Y., Ragauskas, A. & Deng, Y. (2008). Enhanced Enzymatic Hydrolysis of Spruce by Alkaline Pre-treatment at Low Temperature. Biotechnology and Bioengineering. 99(6), 1320-1328.

Zheng, Q., Zhou, T., Wang, Y., Cao, X., Wu, S., Zhao, M., Wang, H., Xu, M., Zheng, B., Zheng, J. & Guan, X. (2018). Pre-treatment of Wheat Starw Leads to Structural Changes and Improved Enzymatic Hydrolysis. *Scientific Reports*, *8*(132), 1-9.

Zheng, Y., Pan, Z., & Zhang, R. (2009) Overview of Biomass Pretreatment for Cellulosic Ethanol Production. *International Journal of Molecular Sciences*. *2*(3), 51-68.