UNIVERSITI PUTRA MALAYSIA

DEVELOPMENT OF INTEGRATED BIOREFINERY MODEL FOR THE PRODUCTION OF BIOETHANOL FROM OIL PALM FROND

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November 2020

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Application of an efficient pretreatment step is crucial in developing a viable biorefinery system for the production of lignocellulosic bioethanol. Subcritical hydrothermal appears as an economic pretreatment method with high sugar recovery. However, there were limited reports on its application with carbon dioxide (CO_2) addition, particularly on oil palm biomass, hence this area should be explored. Moreover, by understanding the mechanism of hemicellulose degradation during pretreatment, the sugar produced hence bioethanol yield could be maximized. Although the integrated biorefinery approach for the production of bioethanol from oil palm frond (OPF) at the oil palm mill was reported promising, assessment of its environmental impact was equally important. Therefore, in this study, subcritical hydrothermal pretreatment of OPF pressed fiber (OPFPF) was conducted using stainless steel tube reactor and miniclave at various temperature, time and CO_2 pressure, to evaluate the effect of CO_2 addition on glucose production. Similarly, a kinetic study was performed to determine the kinetics of hemicellulose (xylan) degradation during the pretreatment using miniclave. In addition, the environmental and economic viability of integrated biorefinery model for bioethanol production from OPF was assessed by Life Cycle Analysis and cost analysis, each, based on three different case studies. Maximum glucose yield of 57.1% (g/g OPFPF) was obtained with application of tube reactor at 180°C, 1 MPa CO_2 for 20 min, and further enhanced to 78.6% using miniclave at similar temperature and pressure for 30 min. Moreover, the rise of temperature and CO_2 addition was found to improve the xylan autohydrolysis, with 180°C and 0.5 MPa CO_2 as the most suitable condition for high glucose recovery from OPFPF. Furthermore, the integrated biorefinery model for the production of bioethanol from the OPF juice offers the best environmental and economic approach with production cost of $0.25/ L. Based on this study, subcritical hydrothermal

pretreatment is a promising method for application at the integrated biorefinery system at the oil palm mill in the future.
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PEMBANGUNAN MODEL LOJI PENAPIS BIO BERSEPADU UNTUK PENGHASILAN BIOETANOL DARIPADA PELEPAH KELAPA SAWIT

Oleh

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Penggunaan langkah prarawatan yang efisien adalah penting dalam membangunkan sistem loji penapis bio berdaya maju untuk penghasilan bioethanol lignoselulosa. Hidroterma subkritikal muncul sebagai kaedah prarawatan yang ekonomi dengan perolehan gula yang tinggi. Walau bagaimanapun, terdapat laporan yang terhad tentang penggunaannya dengan penambahan karbon dioksida (CO_2), terutamanya ke atas biojisim kelapa sawit, maka bahagian ini mesti diterokai. Tambahan pula, dengan memahami mekanisma penyingkiran hemiselulosa semasa prarawatan, penghasilan gula seterusnya bioetanol dapat dimaksimakan. Walaupun pendekatan loji penapis bio bersepadu untuk penghasilan bioetanol daripada pelepah kelapa sawit (OPF) di kilang minyak sawit telah dilaporkan berpotensi, penilaian kesan alam sekitarnya juga adalah penting. Oleh itu, dalam kajian ini, prarawatan hidroterma subkritikal serat mampat pelepah kelapa sawit (OPFPF) telah dijalankan menggunakan reaktor tiub keluli tahan karat dan miniklef pada pelbagai suhu, masa dan tekanan CO_2, untuk menilai kesan penambahan CO_2 ke atas penghasilan glukosa. Begitu juga, kajian kinetik telah dilakukan untuk menentukan kinetik penyingkiran hemiselulosa (xilan) semasa prarawatan menggunakan miniklef. Selain itu, kesauran ekonomi dan alam sekitar model loji penapis bio bersepadu untuk penghasilan bioetanol daripada OPF telah dinilai menggunakan Analisis Kitaran Hidup dan analisis kos, masing-masing, berdasarkan tiga kajian kes yang berbeza. Hasil glukosa tertinggi sebanyak 57.1% (g/g OPFPF) telah diperoleh dengan penggunaan reaktor tiub pada 180°C, 1 MPa CO_2 selama 20 min, dan telah ditingkatkan lagi kepada 78.6% menggunakan miniklef pada suhu dan tekanan sama selama 30 min. Tambahan pula, kenaikan suhu dan penambahan CO_2 telah didapati menambahkan autohidrolisis xilan, dengan 180°C dan 0.5 MPa CO_2 sebagai keadaan paling sesuai untuk perolehan glukosa yang tinggi daripada OPFPF. Selain itu, model loji penapis bio

bersepadu untuk penghasilan bietanol daripada jus OPF menawarkan pendekatan ekonomi dan alam sekitar terbaik dengan kos penghasilan sebanyak $0.25/ L. Berdasarkan kajian ini, prarawatan hidroterma kritikal merupakan kaedah yang berpotensi untuk diaplikasikan pada sistem loji penapis bio bersepadu di kilang minyak sawit pada masa hadapan.

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Declaration by Members of Supervisory Committee

This is to confirm that:

- The research conducted and the writing of this thesis was under our supervision;
- Supervision responsibilities as stated in Rule 41 Rules 2003 (Revision 2012-2013) were adhered to.

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1,4-DB	1,4 dichlorobenzene
ADP	Abiotic resources depletion potential
AFEX	Ammonia fibre explosion
AP	Acidification potential
ARP	Ammonia recycle percolation
BET	Brunauer-Emmett-Teller
BOD	Biochemical Oxygen Demand
Btu	British thermal unit
C_2H_4	Ethylene
CFC-11	Chlorofluorocarbon
CO_2	Carbon dioxide
COD	Chemical Oxygen Demand
CPO	Crude palm oil
CrI	Crystallinity index
CSF	Combined severity factor
DDGS	Dried distiller grain with solubles
DP	Degradation product
E_{ai}	Activation energy
EP	Eutrophication potential
FETP	Freshwater ecotoxicity potential
FFB	Fresh fruit bunches
FGB	First-generation bioethanol
FPU	Filter paper unit
FTIR	Fourier Transform Infrared
g	Gram

GHG	Greenhouse gas
GlcOS	Glucooligosaccharides
GNI	Gross National Income
GWh	Gigawatt hour
GWP	Global warming potential
h	Hour
H_2CO_3	Carbonic acid
H_2O	Water
H_2SO_4	Sulphuric acid
H_3O^+	Hydronium ions
HMF	Hydroxymethylfurfural
HPLC	High Performance Liquid Chromatography
HTP	Human toxicity potential
ISO	International Organization for Standardization
IRR	Internal rate of return
k	Reaction rate constant
kg	Kilogram
kJ	Kilojoule
km	Kilometer
kV	Kilovolt
kWh	Kilowatt hour
L	Liter
LCA	Life cycle analysis
LCB	Lignocellulosic biomass
M	Molar
m	meter

METP	Marine ecotoxicity potential
min	Minute
MJ	Megajoule
mL	Mililiter
NaOH	Sodium hydroxide
NH_3	Ammonia
NO_x	Nitrogen oxides
NREL	National Renewable Energy Laboratory
NPV	Net present value
ODP	Ozone layer depletion potential
OH^-	Hydroxide ions
OPEFB	Oil palm empty fruit bunch
OPF	Oil palm frond
OPFPF	Oil palm frond pressed fiber
OPMF	Oil palm mesocarp fiber
OPT	Oil palm trunk
PKS	Palm kernel shell
PO_4	Phosphate
POCP	Photochemical-oxidant creation potential
POME	Palm oil mill effluent
PV	Pore volume
R	Gas constant
ROI	Return of investment
rpm	Revolutions per minute
s	Second
Sb	Antimony

SEM	Scanning electron microscopy
SGB	Second-generation bioethanol
SO_2	Sulphur dioxide
SSA	Specific surface area
STP	Standard temperature and pressure
TETP	Terrestrial ecotoxicity potential
TGA	Thermal Gravimetric Analysis
v/v	Volume/ volume
VOC	Volatile organic compound
w/w	Weight/ weight
XOS	Xylooligosaccharides
XOS_H	High degree of polymerization XOS
XOS_L	Low degree of polymerization XOS
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Introduction

Total world energy consumption is increasing every year with fossil fuel as the major source of energy supply. In 2015, the total world energy consumption was 575 quadrillions British thermal unit (Btu) and it is projected to achieve 736 quadrillions Btu in 2040 (US Energy Information Administration, 2017). Furthermore, with existing technologies and consumption patterns, the world energy demand is expected to be doubled by the year 2050 (Roy et al., 2012). In order to compensate the increasing energy demand and to lessen the reliability on the depleting fossil fuel, efforts have been directed to the discovery of alternative fuels from renewable resources. According to International Energy Outlook 2016 (US Energy Information Administration, 2016), renewable energy is the world's fastest-growing source of energy, at an average rate of 2.6% per year. This is due to the development of government policies and incentives promoting the use of non-fossil energy sources in many countries.

One of the common technologies for biofuel generation is through the application of microorganism which utilizes carbohydrate as a carbon source. First-generation bioethanol is generated using sugars and starch from feedstocks such as sugarcane and corn (Borrion et al., 2012b; de Souza Dias et al., 2015; Morales et al., 2015; Ometto et al., 2009). However, bioethanol production from lignocellulosic materials including crop residues, forestry and municipal waste is getting much attention these days to overcome the limitation in first-generation biofuel production (Borrion et al., 2012a; Goh et al., 2010b; Kumar and Murthy, 2011). Apart from eliminating competition with a food source, most of these wastes are available in large quantity and cheap. Examples of potential crop residues are wheat straw, sweet sorghum, cane bagasse, oil palm biomass, rice straw and corn stover (Chen and Fu, 2016; Morales et al., 2015; Relvas et al., 2015; Wang et al., 2014b; Zabed et al., 2016). As compared to first-generation biofuel, production of biofuel from non-food feedstocks such as agricultural wastes is more preferable since these wastes are abundantly available and mostly underutilized (Borrion et al., 2012b; Morales et al., 2015).

1.2 Problem statement

Lignocellulosic biomass consists of three major components namely, lignin, hemicellulose and cellulose. These three components existed in a complex manner where they intertwined with each other, forming a sturdy and stable structure. Since hemicellulose and cellulose contributing more than 50% of the total composition, lignocellulosic biomass is considered as a potential source for renewable sugar production. As a second larger palm oil producer in the world, Malaysia generated huge amount of oil palm biomass annually. It was reported that about 51.19 million tonnes of oil palm biomass was produced in Malaysia in 2017 (Hamzah et al., 2019). Oil palm frond (OPF) is among the largest group of oil palm waste with generation of nearly 21.03 million tonnes (dry weight basis) for 95.38 million tonnes of fresh fruit bunch processed in 2014 (Loh, 2017). The petiole of OPF consists of high carbohydrates and nutritive contents and can be converted into value-added products such as biofuels, biobased chemicals, biofertilizer and animal feed (Abdullah et al., 2016; Lee and Ofori-Boateng, 2013a; Ofori-Boateng and Lee, 2014a; Zahari et al., 2015). OPF juice was found to have a high amount of free sugars with 70% of glucose, and can be easily obtained by simple pressing method (Abdullah et al., 2015; Zahari et al., 2014, 2012). Whereas OPF pressed fiber (OPFPF), which is the residual part following pressing, contain a substantial amount of cellulose, approximately 33% - 45%, which can be further hydrolyzed into simple sugars through pretreatment and enzymatic hydrolysis (Goh et al., 2012; Sabiha-Hanim et al., 2011; Xian et al., 2015; Zahari et al., 2014, 2012; Zakaria et al., 2014a). Its availability throughout the year, together with high sugar composition from both OPFPF and its juice, making OPF an outstanding raw material for a feasible biofuel production (Malaysia Innovation Agency, 2013), compared to other oil palm biomass.

The availability of OPF annually and an existing access energy at the oil palm mill offers a great opportunity for the development of an integrated biorefinery for the production of biofuel such as bioethanol at the mill. However, the conversion of OPF to biofuel is challenging due to the complex structure of the lignocellulosic materials. Pretreatments to alter its original structure is necessary before saccharification and fermentation (Abdullah et al., 2016; Borrion et al., 2012b; Morales et al., 2015; Zabed et al., 2016) to break down the complex crystallized structure, making it more accessible for enzyme penetration. Since pretreatment contributed to about 20% of total production cost in cellulosic bioethanol production (Bensah and Mensah, 2013), application of an efficient pretreatment was important to develop a sustainable biorefinery. Subcritical hydrothermal pretreatment offers great advantages where it provides high sugar yield by involving water only, hence eliminates the usage of chemicals (Agbor et al., 2011; Capolupo and Faraco, 2016; Zhuang et al., 2016). Moreover, among all pretreatment method studied, it appears as the most economic method, hence practical for application at the biorefinery system (Harmsen et al., 2010). This could be achieved by utilizing the available excess steam (energy) at the oil palm mill, hence reducing energy waste (Zahari et al., 2015).

Besides that, the presence of subcritical CO_2 as an external promoter during hydrothermal pretreatment was proven to enhance sugar recovery from sugarcane bagasse (Zhang and Wu, 2013, 2014a), wheat straw (Da Silva et al., 2014), eucalyptus (Zhang and Wu, 2014b) and OPMF (Ahmad et al., 2018). The addition of CO_2 is environmentally friendly as it is non-toxic and cheap besides easily separable following application (Morais et al., 2015). In addition, subcritical condition was more preferable as the generation of unwanted sugar degradation products was reduced under mild conditions (Patel et al., 2016; Xiao et al., 2017). Therefore, in this study, subcritical CO_2-H_2O pretreatment was conducted to evaluate the effect of its application on glucose recovery from the OPFPF.

To maximize the sugar produced during saccharification hence bioethanol yield, it is important to understand the effect of certain factors such as temperature on the lignocellulosic material during the hydrothermal pretreatment and the mechanism involved. Kinetic modelling not only helps to understand the mechanism that occurs throughout a process reaction but also provides a theoretical background for improving the operational conditions and subsequent process scale-up in the future (Carvalheiro et al., 2005). Since hemicellulose has a more vulnerable structure compared to cellulose and lignin, it is the most affected part in lignocellulosic material during hydrothermal pretreatment. Hence, most kinetics study was performed, focusing on its degradation (Lei et al., 2013; Relvas et al., 2015). Moreover, it was reported that pretreated solids which are more reactive to enzymatic hydrolysis was generated as more hemicellulose were dissolved (Shao and Lynd, 2013). During hydrothermal pretreatment, hemicellulose particularly xylan was converted into xylooligosaccharides (XOS) and xylose before further degradation occurs at more severe condition, generating furfural and formic acid. It was reported that hemicellulose degradation byproducts such as XOS, xylose, furfural and formic acid were among the compounds which act as inhibitors during enzymatic reaction. Therefore, these compounds must be removed prior to saccharifications by washing or detoxification (Zabed et al., 2017). By studying the mechanisms of hemicellulose degradation, the effect of temperature on xylan degradation could be observed through determination of the reaction rate constants and activation energy. Therefore, the steps that govern the whole reaction at different pretreatment conditions could be identified. Ultimately, this information could be used to determine the condition which is favorable for the generation of glucose production hence increasing the ethanol yield. Furthermore, the generation of unwanted degradation products during subcritical hydrothermal pretreatment could also be reduced. Although the kinetic study of xylan's hydrothermal degradation from a few lignocellulosic materials have been previously reported (Carvalheiro et al., 2005; Relvas et al., 2015), it is important to conduct this study, not only to improve the sugar production from OPFPF, but also to compare the change in the kinetic parameters between different biomass due to the diversity of their compositions. Furthermore, to the best of our knowledge, a limited kinetic study has been reported for the degradation of xylan in OPFPF so far.

Feasibility study on the production of bioethanol from OPF petiole sugars was conducted within an integrated palm biomass biorefinery in the previous (Abdullah et al., 2016). It was demonstrated that integration of a biorefinery to an existing palm oil mill was possible and has high potential for bioethanol production scaling up. However, the environmental criteria must also be considered in developing a sustainable biofuel production process (Morales et al., 2015). LCA is the common method in assessing the environmental performance of a process. Many LCA study has been conducted on biofuel production from various feedstocks and lignocellulosic material over the past years (Borrion et al., 2012b; Morales et al., 2015). It was reported that bioethanol production can contribute to different environmental impacts, depending on the raw material used and process involved (Morales et al., 2015). However, the most highlighted points were the impacts associated with feedstock cultivation and harvesting for first-generation bioethanol (Luo et al., 2009; Muñoz et al., 2014; Ometto et al., 2009) and sugar recovery for lignocellulosic bioethanol production (Borrion et al., 2012b; Wang et al., 2014a) due to chemical (fertilizer), enzyme and fossil fuel usage.

In addition, several studies was also performed on oil palm based biorefinery model for the conversion of different oil palm biomass into various products such as methane gas, compost, ethanol and phytochemicals (Chiew and Shimada, 2013; Harsono et al., 2013; Ofori-Boateng and Lee, 2014b). From these studies, global warming (greenhouse gases) was among the effect reported to be potentially arising from the process involved. Therefore, LCA was performed in this study based on the previous integrated biorefinery model for the production of bioethanol from OPF (Abdullah et al., 2016). Since modifications was also made to improve the performance of the previous model, cost analysis was performed to justify the selection of the best model. Finding of this work could further support the potential of integrating a biorefinery to an existing oil palm mill for the production of biofuel (Abdullah et al., 2016).

1.3 Objectives of the study

This study was conducted based on three objectives, including:

a) To evaluate the effect of subcritical hydrothermal pretreatment with CO_2 addition on glucose recovery from OPFPF.

b) To determine the kinetics of hemicellulose hydrolysis of OPFPF during subcritical hydrothermal pretreatment.

c) To develop and assess the environmental impact and economic viability of an integrated biorefinery approach for bioethanol production from renewable sugars of OPF

1.4 Scope of the study

In general, this study can be divided into three parts according to the objectives. At the beginning of this study, the OPF was pressed using conventional sugarcane pressing machine, generating OPF juice and fiber residues called oil palm pressed fiber (OPFPF). However, only the OPFPF was used for experiments in Objective 1 and Objective 2. Whereas for Objective 3, data used was mostly obtained from the literature review. In the first part of this study, subcritical hydrothermal pretreatment and subcritical CO_2-H_2O of OPFPF was conducted before enzymatic hydrolysis for glucose production. Subcritical hydrothermal pretreatment are process conducted at a condition below critical point of water which is 373°C and 22.1 MPa (Kumar et al., 2018). At subcritical level, the properties of water such as density, viscosity, and dielectric constant dropped compared to at normal condition, making it a suitable medium for solvating organic molecules and higher hydrolysis reaction (Kumar et al., 2018). Two different types of reactors were used which are stainless steel tube reactor, located at the National Institute of Advanced Industrial Science and Technology (AIST), Japan and stainless steel miniclave (Buchi AG, CH-Usher, Switzerland), located in Universiti Putra Malaysia. Initial work was done using stainless tube reactor to get a preliminary data. Due to time limitation, this work was continued using miniclave, with preliminary data as a reference. A mixture of OPFPF and distilled water at a constant solid-liquid ratio of 1:10 was placed in a stainless tube reactor before subcritical hydrothermal pretreatment at different temperature (170 – 200°C), time (10-50 min) and CO_2 initial pressures (0 – 5 MPa). These conditions was designed based on previous subcritical hydrothermal works (Zakaria et al., 2015b; Zhang and Wu, 2014a). Subsequent enzymatic hydrolysis and compositional analysis were conducted according to NREL standard method to observe the difference in glucose production following pretreatment as well as in the lignocellulosic composition of the biomass.

In the attempt to improve the sugar yield, the work was continued using miniclave, based on the preliminary data from hydrothermal pretreatment of OPFPF using tube reactors. 5 g of OPFPF was added into the miniclave at the same solid-liquid ratio, followed by heating at constant temperature of 180°C and initial CO_2 pressure of 1 MPa for several durations (10-50 min) . Then, similar enzymatic hydrolysis and sample analysis was perfomed on the pretreated samples from the miniclave. In order to support the findings, several analyses including Fourier Transport Infrared (FTIR), Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) analysis were conducted on the untreated and treated sample which produced the maximum saccharified sugars.

Meanwhile, for the second part of this work, the trend for xylan conversion into xylooligosaccharides, xylose and degradation products was observed during subcritical hydrothermal pretreatment of OPFPF at two different conditions;

with and without CO_2 addition. Similar model was tested for both conditions since it was demonstrated that the data from CO_2-H_2O pretreatment fitted well with the model proposed earlier by Carvalheiro et al., (2005) for hydrothermal pretreatment (Relvas et al., 2015). Nevertheless, only xylan content was considered in the present study due to low arabinan composition in the OPFPF, making it difficult to obtain the data required to fit into the model. For subcritical hydrothermal pretreatment with CO_2 addition, the temperature and pressure was chosen based on findings from Objective 1 where 180°C and 1 MPa was found to yield the highest glucose production. Hence, findings of this work could also help to explain the glucose yield obtained in Objective 1. However, the variation of initial pressure was limited to 0.5 and 1 MPa only, due to restriction of the reactor used. Since the effects of CO_2 addition was minor due to low CO_2 presence, the kinetic study was continued with experiments without CO_2 addition at four different temperatures (170, 180, 190 and 200°C). Degradation profiles of xylan over 40 minutes treatment time was developed for the experimental and predicted values by using an established degradation model and the kinetic coefficients were then determined.

In the final part of this work, Life Cycle Analysis (LCA) with gate-to-gate approach was performed on conceptual oil palm biorefinery models for the production of bioethanol from renewable sugars of OPF. Three different case studies (A, B and C) were assessed to reduce the environmental impact arising from the production of 1 tonne of bioethanol. The scope of this study includes the transportation of OPF from the plantation to the mill, OPF sugar recovery, fermentation and finally bioethanol purification. Case study A was previously proposed by Abdullah et al., (2016) and it served as a base case. Initially, LCA was conducted on case study A and it was demonstrated that its environmental performance was poor due to application of energy intensive wet disc mill (WDM) for pretreatment of OPFPF and utilization of enzyme. Hence, for case study B, this method was replaced with hydrothermal pretreatment as this method was regarded as more environmental friendly and economic. However, since the glucose yield from subcritical CO_2-H_2O in this work (Objective 1) was low, optimum condition with higher glucose yield for hydrothermal pretreatment of OPFPF reported in the previous was used instead (Zakaria et al., 2015b). On the contrary, only sugar juice was used for bioethanol generation in case study C thus eliminating the need for pretreatment and enzyme usage. Material and energy balance was performed, alongside process simulation using Superpro Designer software for each case study. Ten impact categories were subsequently evaluated based on characterization model of CML 2 baseline 2000 v2.05 incorporated in SimaPro (version 8.0). This characterization model was selected as it is one of the commonly reported model for assessing environmental impact of biofuel generation (Chiew and Shimada, 2013; Dias et al., 2015; Morales et al., 2015; Wang et al., 2014a) To support the findings from the LCA study, cost analysis was also performed on all case studies using the Cost & Evaluation Workbook (Max et al., 2003). The environmental and economical performance between case studies were then compared and discussed.

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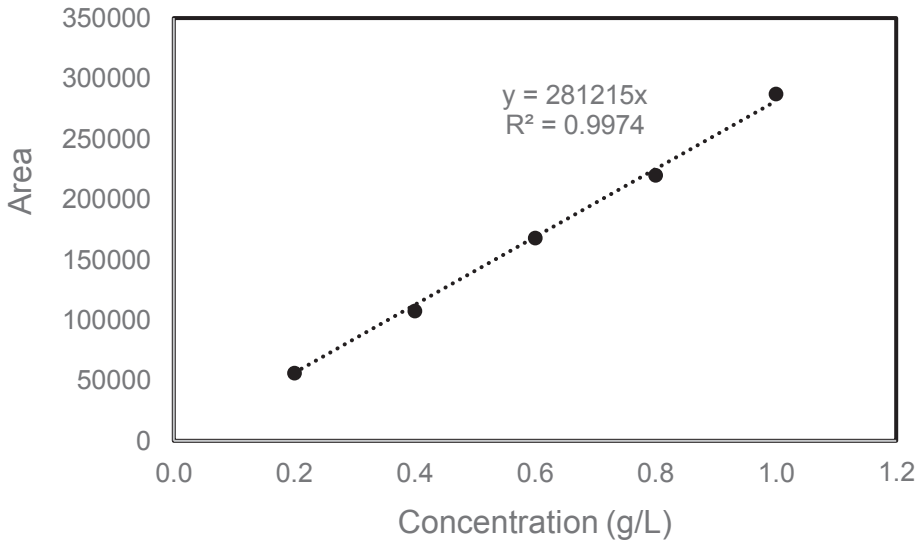
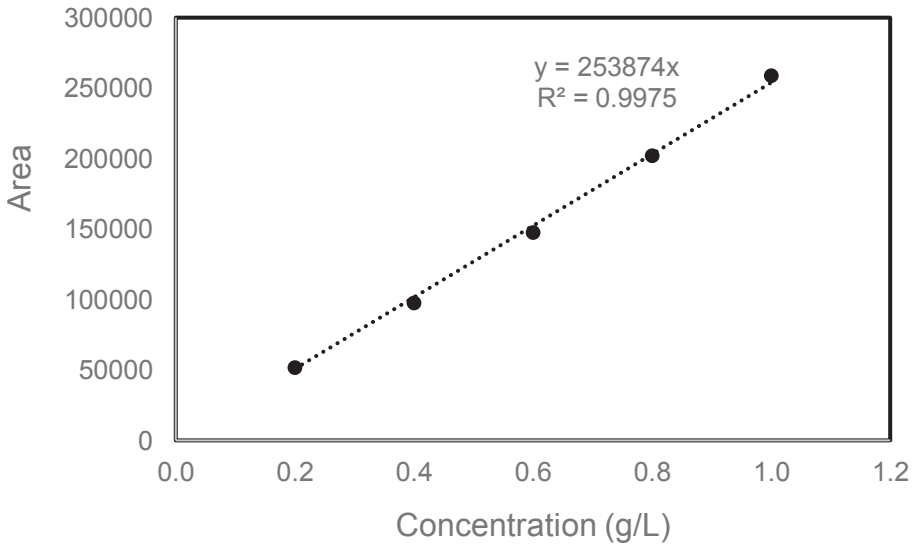
APPENDICES

Appendix A

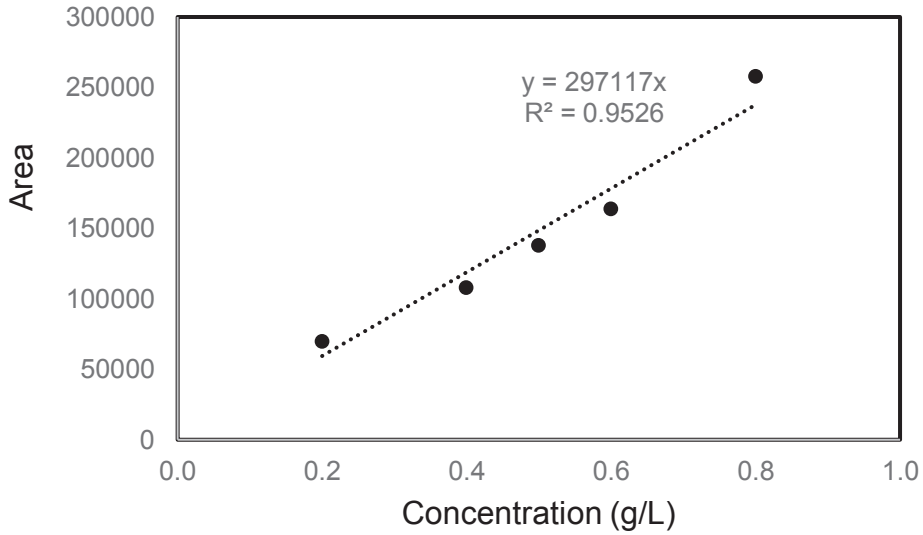
Standard curves for HPLC analysis



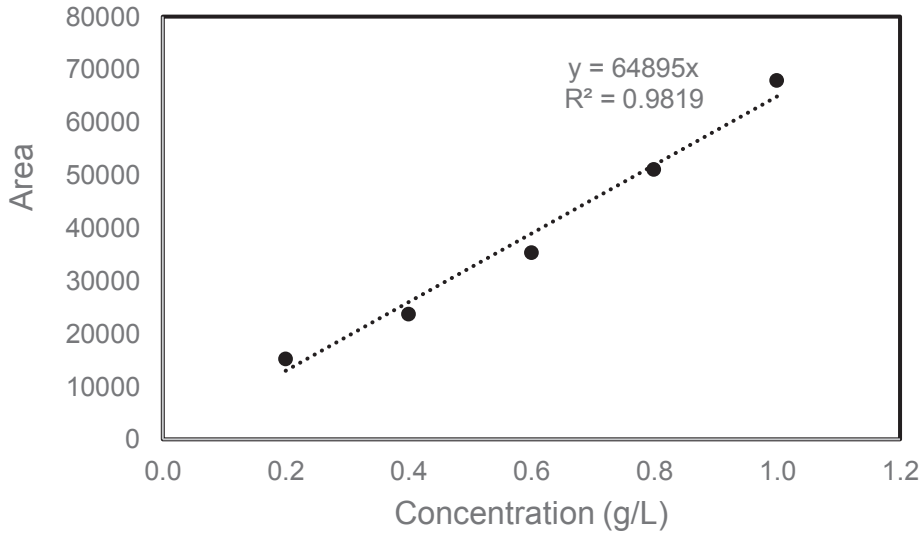
Appendix A.1: Standard curve for glucose concentration



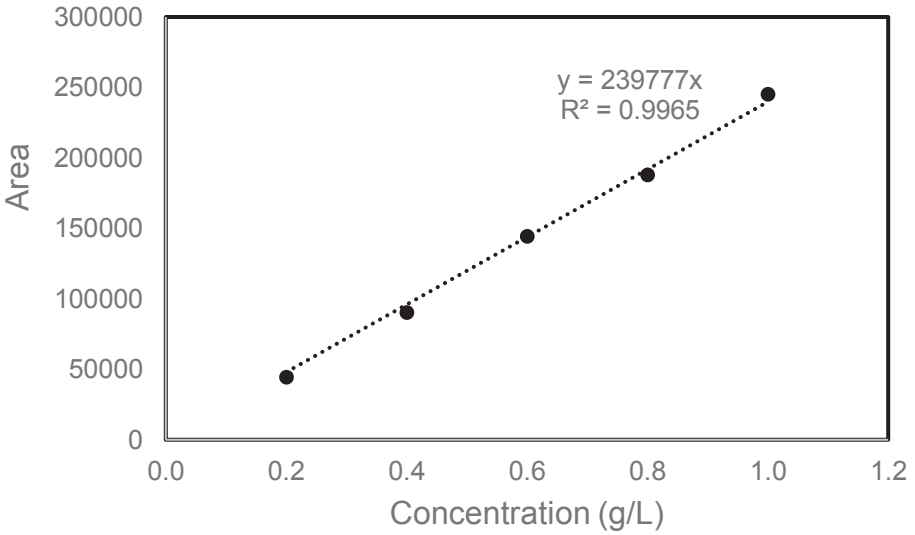
Appendix A.2: Standard curve for xylose concentration



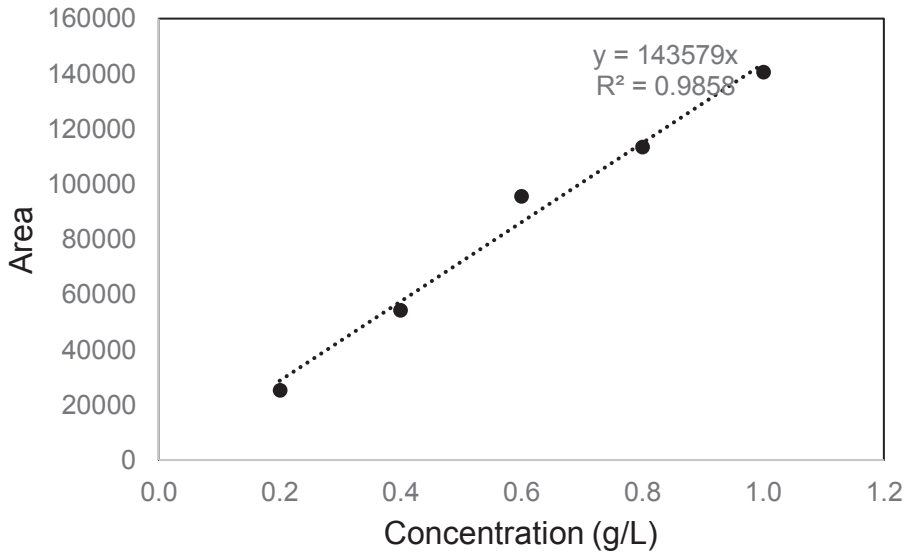
Appendix A.3: Standard curve for arabinose concentration



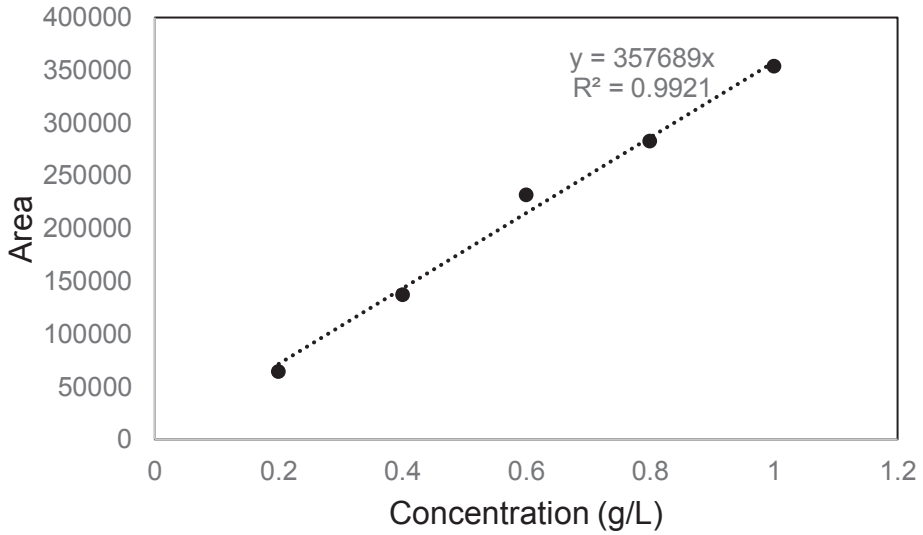
Appendix A.4: Standard curve for galactose concentration



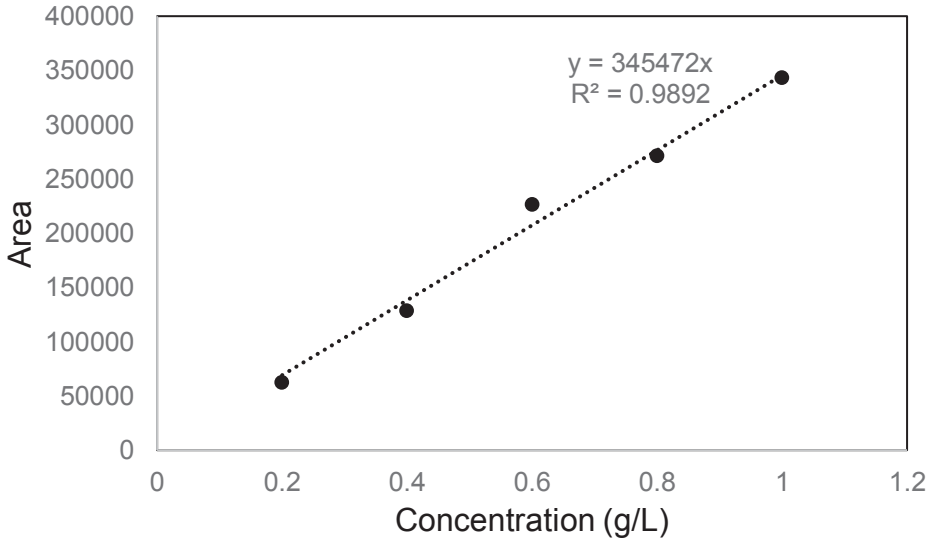
Appendix A.5: Standard curve for mannose concentration



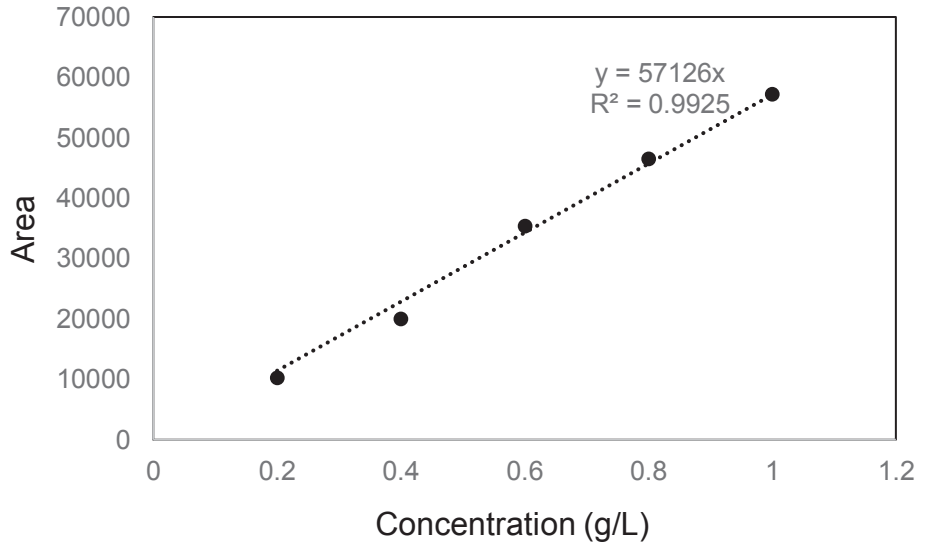
Appendix A.6: Standard curve for acetic acid concentration



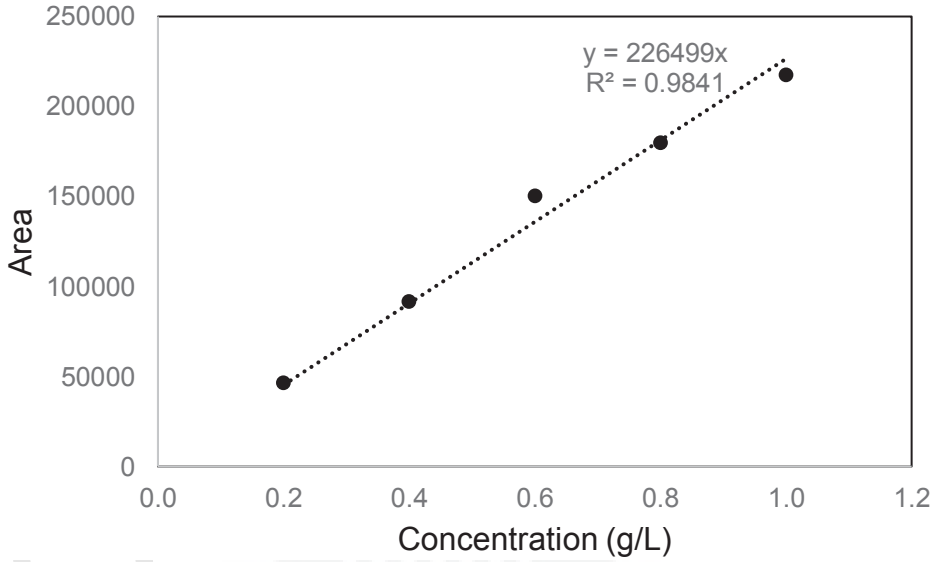
Appendix A.7: Standard curve for 5-HMF concentration



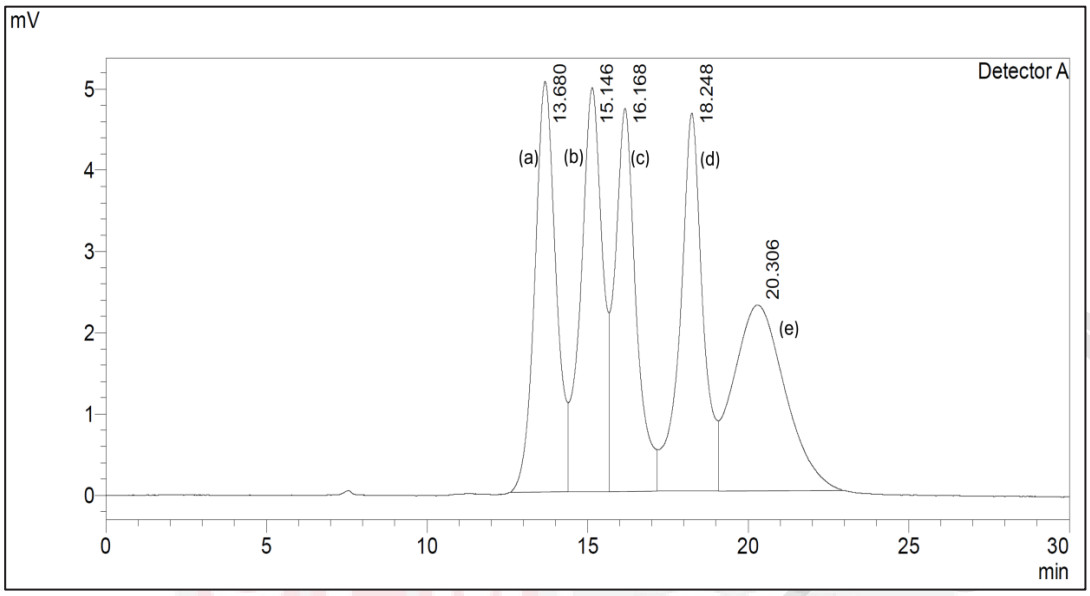
Appendix A.8: Standard curve for furfural concentration



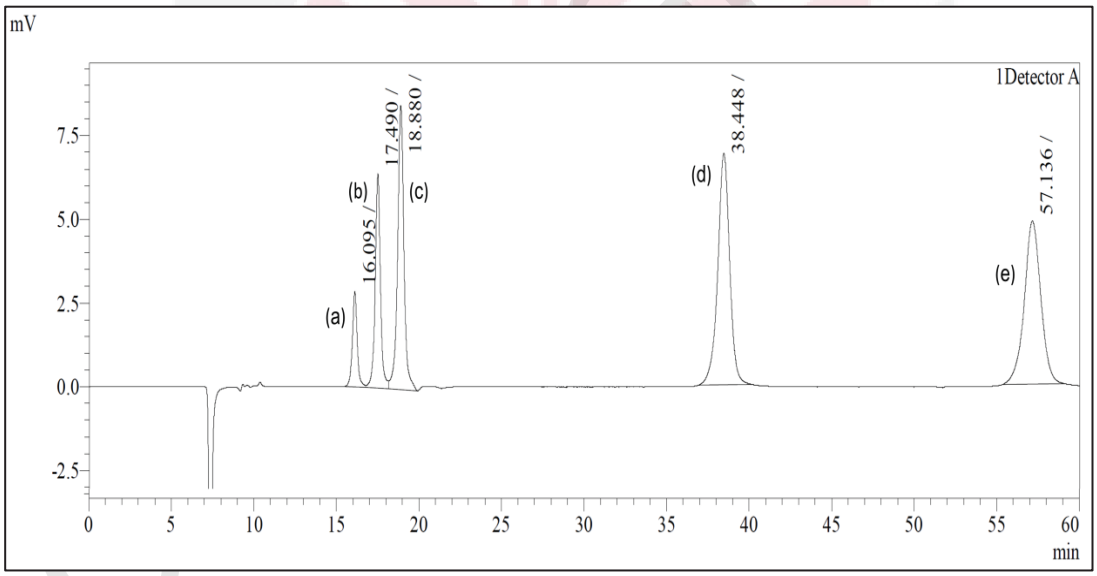
Appendix A.9: Standard curve for formic acid concentration



Appendix A.10: Standard curve for levulinic acid concentration



Appendix A.11: Example of HPLC chromatogram for sugar analysis using Aminex HPX-87P column (Biorad, USA). (a) glucose; (b) xylose; (c) galactose; (d) arabinose; (e) mannose.



Appendix A.12: Example of HPLC chromatogram for inhibitors analysis using Aminex HPX-87H column (Biorad, USA). (a) acetic acid; (b) formic acid; (c) levulinic acid; (d) 5-HMF; (e) furfural.

Appendix B

Equations used for the kinetic study of xylan autohydrolysis

Appendix B.1: Definitions of variables in kinetic model derived equations.

Variables	Definition
Xn_R	The percentage of xylan remaining in the pretreated solid OPFPF, %
Xn_{FS}	The percentage of xylan in the feedstock, %
Xn_0	The percentage of xylan in the pretreated solid OPFPF at the beginning of the set temperature, %
Xn	The percentage of xylan in the pretreated solid OPFPF, %
Xn_{tmax}	The percentage of xylan remaining in the pretreated solid OPFPF at maximum time studied,%
SY	Solid yield, g of solid recovered after treatment per 100 g of feedstock
XOS	Concentrations of xylooligosaccharides in the pretreated liquid, g/L
XOS_R	Percentage of feedstock xylan converted into xylooligosaccharides, %
XOS_H	Percentage of feedstock xylan converted into high molecular weight of xylooligosaccharides, %
XOS_{H0}	Percentage of feedstock xylan converted into high molecular weight xylooligosaccharides at the beginning of the set temperature, %
XOS_L	Percentage of feedstock xylan converted into low molecular weight xylooligosaccharides, %
XOS_{L0}	Percentage of feedstock xylan converted into low molecular weight xylooligosaccharides at the beginning of the set temperature, %
W_L	Weight of the liquid, g
W_{FS}	Weight of the feedstock, g
Xyl	Concentrations of xylose in the pretreated liquid, g/L
Xyl_R	Percentage of feedstock xylan converted into xylose, %
Xyl_0	Percentage of feedstock xylan converted into xylose at the beginning of the set temperature, %
F	Concentrations of furfural in the pretreated liquid, g/L
F_R	The percentage of feedstock xylan converted into furfural, %
F_0	Percentage of feedstock xylan converted into furfural at the beginning of the set temperature, %
DP	Percentage of feedstock xylan converted into degradation products, %
α	Susceptible fraction of xylan
β	Soluble fraction of unreacted xylan
k_i	Reaction rate constant for *i* reaction steps, *i* = 1,2,3,4,5

Appendix B.2: Kinetic model derived equations for calculating experimental values (Carvalheiro et al., 2005; Relvas et al., 2015)**.**

Equation numbers	Equations
B1	$[Xn_R] = \frac{[Xn] \cdot SY}{[Xn_{FS}]}$
B2	$[XOS_R] = \frac{132}{150} \cdot \frac{[XOS] \cdot W_L \cdot 10}{[Xn_{FS}] \cdot W_{FS}}$
B3	$[Xyl_R] = \frac{132}{150} \cdot \frac{[Xyl] \cdot W_L \cdot 10}{[Xn_{FS}] \cdot W_{FS}}$
B4	$[F_R] = \frac{132}{96} \cdot \frac{[F] \cdot W_L \cdot 10}{[Xn_{FS}] \cdot W_{FS}}$
B5	$[DP] = 100 - [Xn] - [XOS] - [Xyl] - [F]$

Appendix B.3: Kinetic model derived equations for calculating predicted values (Carvalheiro et al., 2005; Relvas et al., 2015)**.**

Equation numbers	Equations
B6	$\alpha = \frac{100 - [Xn_{tmax}]}{100}$
B7	$[Xn] = C_1 e^{-k_1 t} + C_2$
B8	$[XOS_H] = C_3 e^{-k_1 t} + C_4 e^{-k_2 t}$
B9	$[XOS_L] = C_5 e^{-k_1 t} + C_6 e^{-k_2 t} + C_7 e^{-k_3 + k6t}$
B10	$[Xyl] = C_8 e^{-k_1 t} + C_9 e^{-k_2 t} + C_{10} e^{-k_3 + k6t} + C_{11} e^{-k_4 t}$
B11	$[F] = C_{12} e^{-k_1 t} + C_{13} e^{-k_2 t} + C_{14} e^{-k_3 + k6t} + C_{15} e^{-k_4 t} + C_{16} e^{-k_5 t}$
B12	$[DP] = 100 - [Xn] - [XOS_H] - [XOS_L] - [Xyl] - [F]$
B13	$C_1 = \beta[Xn_0]$
B14	$C_2 = (1 - \beta)[Xn_0]$
B15	$C_3 = \frac{k_1 C_1}{k_2 - k_1}$
B16	$C_4 = [XOS_{H0}] - C_3$
B17	$C_5 = \frac{k_2 C_3}{k_3 - k_1}$
B18	$C_6 = \frac{k_2 C_4}{k_3 - k_1}$

B19	$C_7 = [XOS_{L0}] - C_5 - C_6$
B20	$C_8 = \frac{k_3 C_5}{k_4 - k_1}$
B21	$C_9 = \frac{k_3 C_6}{k_4 - k_2}$
B22	$C_{10} = \frac{k_3 C_7}{k_4 - k_3}$
B23	$C_{11} = [Xyl_0] - C_8 - C_9 - C_{10}$
B24	$C_{12} = \frac{k_4 C_8}{k_5 - k_1}$
B25	$C_{13} = \frac{k_4 C_9}{k_5 - k_2}$
B26	$C_{14} = \frac{k_4 C_{10}}{k_5 - k_3}$
B27	$C_{15} = \frac{k_4 C_{11}}{k_5 - k_4}$
B28	$C_{16} = [F_0] - C_{12} - C_{13} - C_{14} - C_{15}$
B29	$\beta = 1 - (1 - \alpha)\frac{100}{[Xn_0]}$
B30	$[XOS_R] = [XOS_H] + [XOS_L]$

Appendix C

Calculation step for obtaining energy consumption values in Table 5.3 (Chapter 5)

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1) Milling and juice extraction (Similar values for all case studies)

$$Electricity = 57600\ \frac{tonnes}{year} OPF \times 16 \frac{kWh}{tonne\ OPF} = 0.92\ \frac{GWh}{year}$$

2) Saccharified sugar production (for case study A and B only)

Case study A:

a) Wet disc milling

$$Electricity = 57600\ \frac{tonnes}{year} OPF \times 48 \frac{MJ}{kg\ OPF} \times \frac{0.2778\ kWh}{1\ MJ}$$
$$= 268.8 \frac{GWh}{year}$$

b) Saccharification

$$Electricity = 28800\ \frac{tonnes}{year} wet\ OPFPF \times 24 \frac{kWh}{tonne\ wet\ OPFPF}$$
$$= 0.69\ \frac{GWh}{year}$$

c) MVR evaporator

$$Electricity = 20160\ \frac{tonnes}{year} dried\ OPFPF \times 43.4 \frac{kWh}{tonne\ dried\ OPFPF} = 0.87\ \frac{GWh}{year}$$

$$Steam = 20160\ \frac{tonnes}{year} dried\ OPFPF \times 18.7 \frac{kg}{tonne\ dried\ OPFPF}$$
$$= 380\ \frac{tonne}{year}$$

Hence,

$$Total\ electricity = 269 + 0.69 + 0.87 = 270.56\ GWh/year$$
$$Total\ steam = 380 \frac{tonne}{year}$$

Case Study B

a) Grinding

$$Electricity = 20160\ \frac{tonnes}{year} dried\ OPF\ \times 30 \frac{kWh}{tonne\ OPF}$$
$$= 0.60\ \frac{GWh}{year}$$

b) Hydrothermal pretreatment
Using the equation from Hosseini and Shah (2009),

$$E = 1.2(1112.0 + 4.85T_2)(T_2 - T_1)$$

Where,
$E\ is\ energy\ (J/kg)$,
$1.2\ is\ heat\ loss$,
$(1112.0 + 4.85T_2)\ is\ the\ specific\ heat\ capacity\ of\ wood\ (J/kg \cdot K)$,
$T_2\ is\ final\ heating\ temperature\ (210℃ = 483.15\ K)$,
$T_1\ is\ initial\ temperature (20℃ = 293.15\ K)$

Hence,

$$E = 1.2(1112.0 + 4.85(483.15K)(483.15 - 293.15) = 787.8\ \frac{kJ}{kg}$$

For 20160 tonne of dried OPFPF,

$$E = 787.8 \frac{kJ}{kg} \times 20160\ \frac{tonne}{year} = 1.59 \times 10^{10} \frac{kJ}{year}$$

Latent heat of vaporization of steam at 20 bar is 1888.65 kJ/kg. Hence, the amount of steam required for hydrothermal pretreatment;

$$Steam = \frac{1.59 \times 10^{10}\ \frac{kJ}{year}}{1888.65\ \frac{kJ}{kg}} = 8418.7\ \frac{tonne}{year}$$

Amount of HP steam generated (20 bar) at the mill is **299325** tonne/year; and

299325 tonne of HP steam generates 7.72 GWh of electricity.

Electricity usage at the mill is 4.08 GWh. The amount of HP steam required to generate 4.08 GWh is;

$$Steam = \frac{4.08\ GWh\ x\ 1000x1000\ x\ 0.774}{1\ kWh/30\ kg} = 175711\ tonne/year$$

For bioethanol production, requires 2.61 GWh of electricity. The amount of HP steam required to generate 2.61 GWh is;

$$Steam = \frac{2.61\ GWh\ x\ 1000\ x1000\ x\ 0.774}{1\ kWh/30\ kg} = 112403\ tonne/year$$

Therefore, total HP steam required for electricity generation is,
$HP\ steam\ required\ = 175711 + 112403 = \mathbf{288114}\ tonne/year$
Hence,

$$Remaining\ HP\ steam = 299325 - 288114 = 11211\ tonne/year$$

Since only 8418.7 tonne/year of HP steam is required for conducting hydrothermal pretreatment, the remaining HP steam is sufficient. It is therefore suggested to tap the HP steam from the current existing channel (as indicated in **Figure 5.6**).

c) Saccharification
Using solid recovery of 52.2% (Zakaria et al., 2015b), the amount of OPFPF generated following hydrothermal pretreatment was 10523.5 tonnes/year. Therefore, in saccharification,

$$Electricity = 10523.5\ \frac{tonnes}{year}\ OPFPF\ \times 24 \frac{kWh}{tonne\ OPFPF}$$
$$= 0.25\ \frac{GWh}{year}$$

d) MVR evaporator
$Electricity = 10523.5\ \frac{tonnes}{year} dried\ OPFPF\ \times$
$43.4 \frac{kWh}{tonne\ dried\ OPFPF} = 0.46\ \frac{GWh}{year}$

$$Steam = 10523.5\ \frac{tonnes}{year} dried\ OPFPF\ \times 18.7 \frac{kg}{tonne\ dried\ OPFPF}$$
$$= 197\ \frac{tonne}{year}$$

Hence,
$Total\ electricity = 0.60 + 0.25\ +\ 0.46 = 1.31\ GWh/year$
$$Total\ steam = 197 + 8419 = 8616 \frac{tonne}{year}$$

3) OPF juice pretreatment (Similar values for all case studies)
3 multiple effect evaporator:

$$Steam = 57600\ \frac{tonnes}{year}\ OPF\ \times 86.6 \frac{kg}{tonne\ \ OPF} = 4988\ \frac{tonne}{year}$$

4) Fermentation

Case study A

a) Sterilization

$$Steam = 55600\ \frac{tonnes}{year}\ OPF\ sugar\ \times 563 \frac{kg}{tonne\ \ sugar}$$
$$= 31300\ \frac{tonne}{year}$$

b) Fermenter

$$Electricity = 55600\ \frac{tonnes}{year} OPF\ sugar\ \times 12 \frac{kWh}{tonne\ sugar}$$
$$= 0.67\ \frac{GWh}{year}$$

Case study B

a) Sterilization

$$Steam = 31364\ \frac{tonnes}{year}\ OPF\ sugar\ \times 563 \frac{kg}{tonne\ \ sugar}$$
$$= 17660\ \frac{tonne}{year}$$

b) Fermenter

$$Electricity = 31364\ \frac{tonnes}{year} OPF\ sugar\ \times 12 \frac{kWh}{tonne\ sugar}$$
$$= 0.38\ \frac{GWh}{year}$$

Case study C

a) Sterilization

$$Steam = 8400\ \frac{tonnes}{year}\ OPF\ sugar\ \times 563 \frac{kg}{tonne\ \ sugar}$$
$$= 4730\ \frac{tonne}{year}$$

b) Fermenter

$$Electricity = 8400\ \frac{tonnes}{year} OPF\ sugar\ \times 12 \frac{kWh}{tonne\ sugar}$$
$$= 0.10\ \frac{GWh}{year}$$

5) Ethanol purification

Case study A

$$Steam = 26700\ \frac{tonnes}{year} C_2H_5OH\ \times \frac{10^3 L}{789\ kg} \times 2.55 \frac{kg}{L\ \ C_2H_5OH}$$
$$= 86300\ \frac{tonne}{year}$$

Case study B

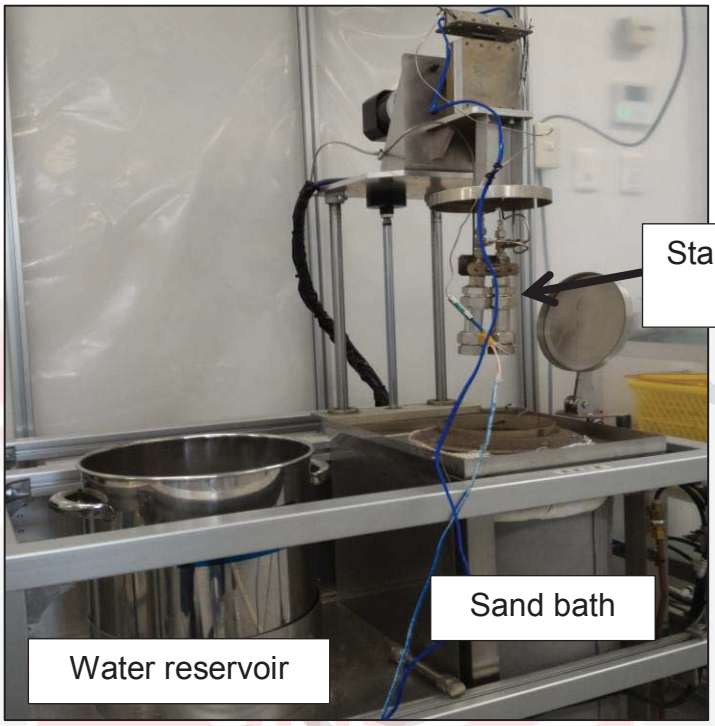
$$Steam = \ 15000 \ \frac{tonnes}{year} C_2H_5OH \ \times \frac{10^3 L}{789 \ kg} \times 2.55 \frac{kg}{L \ C_2H_5OH}$$
$$= 48500 \ \frac{tonne}{year}$$

Case study C

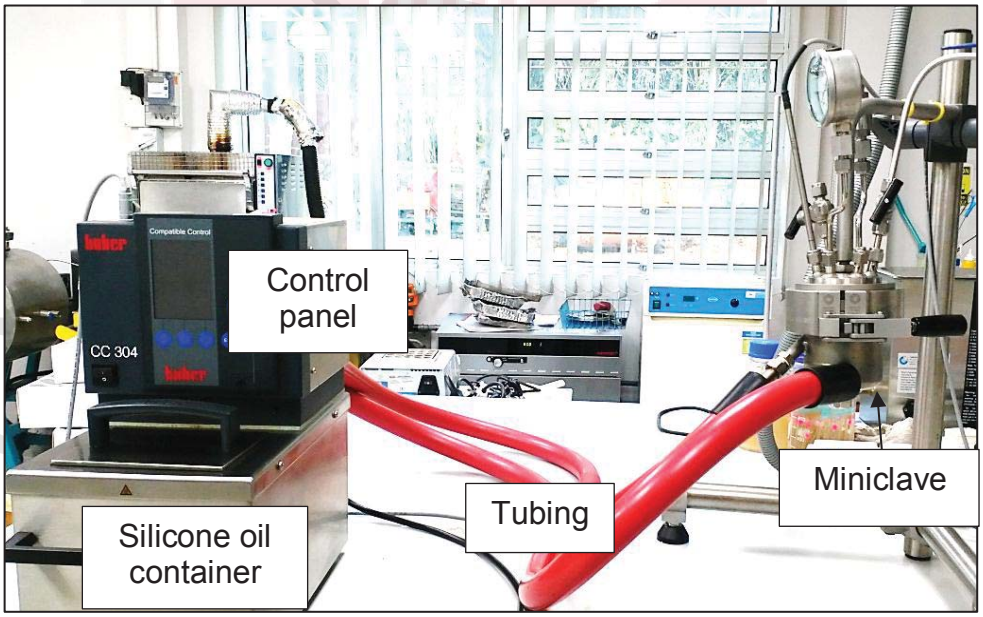
$$Steam = \ 4000 \ \frac{tonnes}{year} C_2H_5OH \ \times \frac{10^3 L}{789 \ kg} \times 2.55 \frac{kg}{L \ C_2H_5OH}$$
$$= 13000 \ \frac{tonne}{year}$$

Appendix D

Picture of subcritical hydrothermal reactors



Appendix D.1: Stainless steel tube reactor



Appendix D.2: Miniclave

BIODATA OF STUDENT

Siti Jamilah Hanim Mohd Yusof was born on June 8, 1981 in Hospital Terendak, Malacca. She received her early education at Sekolah Kebangsaan Klang Gate, Gombak, Selangor (1988 to 1992) and Sekolah Kebangsaan Ampangan, Seremban, Negeri Sembilan (1993). She continued her secondary education at Sekolah Menengah Agama Persekutuan, Labu, Negeri Sembilan from 1994 until 1998. Later, in 1999, she went to Universiti Kebangsaan Malaysia, Bangi, Selangor for one year matriculation program. After completion of her matriculation program, she continued her First Degree in Bachelor of Chemical Engineering, a four year program at the same university and graduated in 2005. In 2007, she pursued her Master's Degree in the engineering field under supervision of Prof. Ir. Dr. Mohd Sobri Takriff in UKM and financially supported by Universiti Malaysia Perlis (UniMAP) and Ministry of Higher Education (MOHE) under Skim Latihan Akademik Bumiputera (SLAB). Upon completion of her study in 2011, she was appointed as a lecturer at School of Bioprocess Engineering, Universiti Malaysia Perlis, Perlis. After 3 years of working, she pursued her PhD study in October 2014 at Universiti Putra Malaysia under supervision of Prof. Dato' Dr. Mohd Ali Hassan in the field of Biochemical Engineering. During her entire postgraduate study, besides sponsorship from MOHE and UniMAP, she had also received sponsorships from Japan International Cooperation Agency (JICA) to conduct a research project at the National Institute of Advanced Industrial Science and Technology, Hiroshima, Japan from August to September 2015. The result of her research is as presented in this thesis.

LIST OF PUBLICATIONS

Journal and Book Chapter

Yusof, S. J. H. M., Roslan, A. M., Ibrahim, K. N., Abdullah, S. S. S., Zakaria, M. R., Hassan, M. A., Shirai, Y., Life cycle assessment for bioethanol production from oil palm frond juice in an oil palm based biorefinery. Sustainability, 2019, 11, 1-14.

Yusof, S. J. H. M., Zakaria, M. R., Roslan, A. M., Ali, A. A. M., Shirai, Y., Ariffin, H., Hassan, M. A., Oil palm biomass biorefinery for future bioeconomy in Malaysia. In book: Lignocellulose for Future Bioeconomy, 2019, Elsevier.

Conference Proceeding and Abstracts

Yusof, S. J. H. M., Roslan, A. M.,Fujimoto, S., Zakaria, M. R., Hassan, M. A., Shirai, Y., Production of Xylooligosaccharides by Carbon Dioxide-Assisted Hydrothermal Pretreatment of Oil Palm Biomass. In: The Asian Federation of Biotechnology Malaysia Chapter International Symposium 2019 (AFOBMCIS 2019), Hotel Bangi Putrajaya, Selangor, Malaysia.

Yusof, S. J. H. M., Roslan, A. M., Ibrahim, K. N., Abdullah, S. S. S., Zakaria, M. R., Hassan, M. A., Shirai, Y., Life Cycle Assessment of Bioethanol Production From Oil Palm Frond in Oil Palm Based Biorefinery. In: Symposium of Applied Engineering and Sciences 2019 (SAES 2019), Universiti Putra Malaysia, Selangor.

Yusof, S. J. H. M., Roslan, A. M., Ibrahim, K. N., Abdullah, S. S. S., Zakaria, M. R., Hassan, M. A., Shirai, Y., Environmental performance of bioethanol production from oil palm frond petiole sugars in an integrated palm biomass biorefinery. IOP Conf. Series: Materials Science and Engineering, 2018, 368, (2018) 012004.