LIGNOCELLULOSIC BIOMASS FROM AGRICULTURAL RESIDUE FOR THE PRODUCTION OF BIOENERGY AND BIO-BASED MATERIALS

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by

SAIMA SOHNI

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

AIL	Acid insoluble lignin
ASL	Acid soluble lignin
ASTM	American society for testing and materials
BET	Brunauer-Emmett-Teller
BJH	Barrett−Joyner−Halenda
Chit/L_{NP}	Chitosan/nano-lignin
CHNS/O	Carbon, hydrogen, nitrogen, sulphur and oxygen
CrI	Crystallinity index
DNS	3,5-dinitrosalicylic acid
DTG	Differential thermogravimetry
EFB	Empty fruit bunch
FAO	Food and agriculture organization
FC	Fixed carbon
FPU	Filter paper unit
FTIR	Fourier-transform infrared spectroscopy
HHV	Higher heating value
HPLC	High performance liquid chromatography
KF	Kenaf stalk
L_{NP}	Nanoparticles of polymer lignin
MB	Methylene blue
MIGHT	Malaysian industry group for high technology
MPa	Megapascal
MPI	Ministry of primary industry

MPOB	Malaysian palm oil board
NKTB	National kenaf and tobacco board
NREL	National renewable energy laboratory
OPF	Oil palm frond
OPT	Oil palm trunk
PKC	Palm kernel cake
PKS	Palm kernel shell
POME	Palm oil mill effluents
PPF	Palm pressed fiber
q_o	Theoretical maximum of adsorption capacity
RH	Rice husk
RS	Rice straw
SC-CO_2	Supercritical carbondioxide
SEM	Scanning electron microscopy
TAPPI	Technical association of pulp and paper industry
TG	Thermogravimetry
THF	Tetrahydrofuran
T_{max}	Temperature at maximum rate of decomposition
UV-VIS	Ultraviolet-visible
VM	Volatile matter
XRD	X-ray diffraction
XRF	X-ray fluorescence
λ_{max}	Wavelength of maximum absorbance

BIOJISIM LIGNOSELULOSIK DARIPADA SISA PERTANIAN UNTUK PENGHASILAN BIO TENAGA DAN BAHAN BERASASKAN BIO

ABSTRAK

Objektif kajian ini adalah mengkaji sifat-sifat kimiafizik biojisim lignoselulosik di Malaysia untuk memastikan kesesuaian dan penggunaannya untuk pemprosesan hiliran sebagai bahan mentah berpotensi untuk penghasilan biotenaga dan bahan berasaskan bio. Kajian ini terdiri daripada tiga fasa. Pada fasa pertama, pencirian sifat-sifat kima-fizik dilakukan terhadap dahan kelapa sawit (OPF), batang kelapa sawit (OPT), tandan buah kosong (EFB), cangkerang isi kelapa sawit (PKS), sekam padi (RH) jerami padi (RS) dan kenaf (KF). Kajian ini berasaskan penentuan komposisi proksimat, kandungan CHNS/O, nilai kalori dan penentuan kandungan lignoselulosa. Sebagai tambahan, pelbagai teknik-teknik analitikal seperti Fourier transformasi inframerah (FTIR), analisis pembelauan sinar-X (XRD), analisis spektoskopi pendarfluor sinar-X (XRF) dan analisis termal gravimetrik digunakan untuk mengkaji sifat-sifat seperti kumpulan berfungsi, struktur penghabluran, komposisi mineral, dan degradasi termal bagi bahan-bahan tersebut. Data daripada fasa pertama memberikan garisan dasar untuk fasa seterusnya dimana dua kaedah pemprosesan mesra alam baru digunakan untuk OPT dan PKS iaitu superkritikal karbon dioksida (SC-CO_2) dan kaedah tetrahidrofuran (THF). Keputusan menunjukkan bahawa daripada segi jirim meruap, mengikut turutan adalah; EFB (83.42%) > KF (82.70%) > OPT (81.46%) > OPF (76.98%) > RS (76.42%) > PKS (69.66%) > RH (66.65%), menunjukkan hasil dalam penukaran termokimia. Analisis proksimat menunjukkan bahawa RH mempunyai kandungan abu tertinggi (18.82%), terutamanya kandungan silika. Kandungan minimum bahan abu dihasilkan oleh KF (5.73%), EFB (6.56%) dan OPT (7.71%) yang mengandungi pecahan tinggi spesies

pemangkin yang berkemungkinan turut serta dalam reaksi pirolitik. PKS memberikan potensi termokimia maksimum dengan nilai pemanasan yang lebih tinggi iaitu 17.32 MJ/kg diikuti oleh KF (16.66 MJ/kg), OPT (16.34 MJ/kg), RS (16.15 MJ/kg), EFB (16.07 MJ/kg) 14.49 MJ/kg) dan RH (14.37 MJ/kg). Analisis komposisi menunjukkan bahawa OPT, OPF dan KF kaya dengan kandungan polisakarida dengan kuantiti lignin yang kurang, justeru menjadi bahan berharga untuk aplikasi bahan gentian dan penukaran-bio. Kandungan lignin tertinggi didapati dalam PKS, justeru boleh dieksploitasi dalam pembuatan komposit berasaskan lignin. Berdasarkan saringan awal, biojisim OPT dikenalpasti sebagai bahan mentah untuk penukaran-bio dan prosesnya menggunakan SC-CO_2 yang menunjukkan perubahan ketara dalam sifat-sifat kimiafizik untuk pecahan OPT terawat berbanding OPT tidak dirawat. Penukaran selulosa terbaik iaitu 61.14% dicapai pada enzim 80 FPU/g glukan selepas pencernaan 72 jam untuk SC-CO_2 OPT terawat dengan kondisi proses yang dikawal; T =80°C, P= 35MPa, M = 60% dan t =60min berbanding 37.09%. Berdasarkan saringan awal, PKS yang kaya dengan lignin diproses menggunakan kaedah THF menghasilkan formasi langsung nanosfera berongga dengan turutaan dimensi 138 nm. Penambahan L_{NP} dalam matriks kitosan menunjukkan perubahan ketara dalam sifat-sifat kimiafizik komposit kitosan/nano-lignin berbanding perintis. Ini disebabkan oleh kesan sinergi saiz tertentu (kesan-nano) dan penambahan kefungsian disebabkan oleh L_{NP} dalam bio-nanokomposit. Kesimpulannya, kajian ini boleh menyumbang kepada pemahaman yang lebih baik mengenai pengaruh faktor-faktor yang berbeza yang berkaitan dengan biojisim, sifat-sifat kimiafizik, potensi sebagai bahan mentah yang baru untuk bio-tenaga dan bahan berasakan bio, dan juga mempromosikan teknologi hijau dalam pemprosesan biojisim untuk penapisan-bio.

LIGNOCELLULOSIC BIOMASS FROM AGRICULTURAL RESIDUE FOR THE PRODUCTION OF BIOENERGY AND BIO-BASED MATERIALS

ABSTRACT

The objectives of this study are to investigate physicochemical properties of wide range of agricultural residues available in Malaysia to ascertain their suitability for downstream processing along with prospective usage as promising feedstock in the production of bioenergy and bio-based materials. In the first phase, physicochemical characterization was carried out for oil palm frond (OPF), oil palm trunk (OPT), oil palm empty fruit bunch (EFB), oil palm kernel shell (PKS), rice husk (RH), rice straw (RS) and kenaf stalk (KF). These studies were based on proximate composition, CHNS/O content, calorific value and lignocellulosic content determination. In addition, various analytical techniques such as Fourier transform infrared (FTIR), X-ray diffraction (XRD), X-ray fluorescence (XRF) spectroscopy and thermogravimetry (TGA) were used to study microscopic properties such as functional groups, crystallographic structure, mineralogical composition and thermal degradation, respectively of these residues. Results of the first phase provided baseline for subsequent phases wherein two new eco-friendly processing methods using supercritical carbondioxide (SC-CO_2) and tetrahydrofuran (THF) were demonstrated for OPT and PKS, respectively. Results of the first phase showed that in terms of volatile matter, the order followed was; EFB (83.42 %) > KF (82.70 %) > OPT (81.46 %) > OPF (76.98 %) > RS (76.42 %) > PKS (69.66 %) > RH (66.65 %), showing yield in thermochemical conversion. Proximate analysis revealed that RH has the highest ash content (18.82 %), predominantly composed of silica. The minimum ash material was generated by KF (5.73 %), EFB (6.56 %) and OPT (7.71 %), containing high fractions of catalytic species which are likely to participate in pyrolytic reactions. The

PKS presented maximum thermochemical potential with higher heating value of 17.32 MJ/kg followed by KF (16.66 MJ/kg), OPT (16.34 MJ/kg), RS (16.15 MJ/kg), EFB (16.07 MJ/kg), OPF (14.49 MJ/kg) and RH (14.37 MJ/kg). Compositional analysis revealed that OPT, OPF and KF were rich in polysaccharide content with much less quantity of lignin (<30 %), hence are valuable for fiber application and bioconversion. The maximum content of lignin was found in PKS, hence can be exploited in fabricating lignin-based composites. Based on initial screening, OPT biomass was identified as an ideal feedstock for bioconversion and its processing using SC-CO_2 resulted in marked changes in physicochemical properties of treated OPT fractions, as compared to untreated OPT. The best cellulose conversion of 61.14 % was achieved at enzyme loading of 80 FPU/g of glucan after 72 h digestion for SC-CO_2 treated OPT under process conditions; T = 80 °C, P = 35 MPa, moisture = 60 % and t = 60 min as compared to 37.09 % in control. Based on initial screening, PKS being rich source of lignin was processed using THF-based method which resulted in the direct formation of lignin hollow nanospheres (L_{NP}) with dimension of the order of 138±39 nm. The inclusion of L_{NP} in chitosan matrix resulted in marked changes in physicochemical properties of chitosan/nano-lignin composite as compared to precursor. This can be attributed to synergistic effects of size particularity (nano-effect) and incorporated functionalities due to L_{NP} in bionanocomposite. As-prepared composite showed excellent performance as innovative adsorptive platform, as demonstrated by efficient removal (~83 %) of model dye. In conclusion, these investigations could decisively contribute to a better understanding of the influence of different factors related to biomass residues on their physicochemical properties and candidacy as renewable feedstock for bioenergy and bio-based materials, as well as in promoting green technologies for biomass processing in biorefinery.

CHAPTER 1

INTRODUCTION

1.1 Research background

Agricultural development on sustainable basis has led to a rise in the generation of large quantity of lignocellulosic biomass residues in Malaysia. For example, agricultural residues from oil palm (oil palm frond, oil palm trunk, oil palm empty fruit bunch, oil palm kernel shell and palm pressed fiber) (Salema et al., 2019), paddy (rice husk and rice straw) (Loy et al., 2018), kenaf (kenaf stalk, pith and bark) (Devadas et al., 2018) crops and so forth, are the readily available lignocellulosic biomass materials. According to the Malaysian Industry Group for High Technology (MIGHT), these residues are also covered under strategic action plan 2020 for developing and promoting stakeholders in implementing sustainable production through participation in the Malaysian biomass industry (MIGHT, 2013).

The development of agricultural sector has been anticipated to remain strong in the next few decades due to economic development and population growth, with the consequence that the quantity of agricultural wastes would essentially remain high in Malaysia. The traditional approaches of biomass waste recycling including open field disposal (Uemura et al., 2013), compositing (Krishnan et al., 2017) and mulching (Moradi et al., 2015) are not only inadequate with no economic advantages, but also can be a significant source of environmental deterioration apparently because of its negative effect on the land and the surrounding regions, and at the same time can damage the quality of air and water (Bruckman, 2016).

Globally, research interest in utilizing lignocellulosic biomass as renewable feedstock in a biorefinery has gained momentum for wide array of downstream utilizations, for instance bioenergy, bio-based materials etc. Lignocellulosic biomasses are promising resources essentially because they are the most abundant, carbon neutral and low-cost with no food vs. fuel competition (Sánchez et al., 2019). In principle, the conversion of biomass into useful materials covers a wide range of different types and sources of biomass (Sahoo et al., 2019), conversion options (Kellock et al., 2019, Alvarez et al., 2019, Zhou et al., 2018, Sui et al., 2019, Avelino et al., 2018, Zhang et al., 2018), end-use applications (Martínez-Patiño et al., 2018, Patel et al., 2018, Alqahtani et al., 2019, Mohammed et al., 2019) and infrastructure requirements (Aboelazayem et al., 2018, Polin et al., 2019, Monir et al., 2018). Till today, conversion of lignocellulosic biomass is an emerging sector, with unanswered questions relating to the choice of feedstocks, economical processing, and identification of viable end products that will lead to sustainable development of this industry (Hassan et al., 2019).

The lignocellulosic biomass possesses a highly complex heterostructure primarily composed of cellulose, hemicellulose, lignin along with some inorganic components (Li et al., 2016) and to be useful in various applications requires efficient separation of these constituents (Yamaguchi et al., 2019). This has two implications from biorefinery perspective. Firstly, physicochemical charcaterization of lignocellulosic biomass becomes essential because the presence of these components in different proportion confers unique properties to each lignocellulosic biomass (Marrugo et al., 2016). Secondly, there is a need for appropriate biomass processing to deconstruct and refine it into its major components for wide variety of downstream utilizations (Zhou et al., 2017, Cornejo et al., 2019, Ji et al., 2018).

As the lignocellulosic biomass is generated in massive quantity, the ability to conduct systematic characterization of all kinds of properties, such as chemical, structural, physical and mechanical attributes using analytical instruments is essential in order to take full advantage of biomass in developing innovative uses (Satyanarayana et al., 2007, Foston and Ragauskas, 2012). Globally, substantial amount of research on physicochemical properties of lignocellulosic biomasses has been carried out. For example, aiming to use natural fibers as reinforcing agents in polymers, (Spinace et al., 2009) studied and characterized native and pretreated curaua fibers in terms of chemical, structural and mechanical properties. In another study, (Neto et al., 2013) performed comparative evaluation of structural, chemical, thermal, mechanical and morphological properties of different pineapple leaf fiber varieties for prospective use in composites. Similar studies were also carried out on lignocellulosic biomasses available in China (Cuiping et al., 2004), North America (Nanda et al., 2013), India (Raj et al., 2015, Singh et al., 2017, Shah et al., 2018, Mishra and Mohanty, 2018), Colombia (Marrugo et al., 2016) and Brazil (de Paula Protásio et al., 2013, Pereira et al., 2016) for their biofuel potential. In Malaysia, it was noticed that such studies are meant for a very specific role and are available in isolated forms. For example, (Abdul Khalil et al., 2008) studied oil palm empty fruit bunch, oil palm frond and oil palm trunk to provide a better understanding of their morphology and composition. The production and characterization of biochar derived from oil palm kernel shell was reported by (Kong et al., 2013). Similarly, pyrolysis of selected biomass was undertaken to investigate its correlation with the physicochemical properties of ashes for potential utilization as crude fertilizer or cement replacement material from oil palm empty fruit bunch (Yin et al., 2008), C-sequestration and soil amendment using rice husk (Naqvi et al., 2015). Similar study was done on biochar derived from gasified oil palm frond, oil palm trunk and oil palm empty fruit bunch by (Mahmood et al., 2015). Furthermore, (Abdullah et al., 2010, Abdullah and Yusup, 2010) studied physicochemical properties of agricultural residues for potential hydrogen generation. The oil palm empty fruit bunch was evaluated for its thermochemical potential by (Omar et al., 2011, Mohammed et al., 2012, Abnisa et al., 2013). In another study, (Sabil et al., 2013) assessed the influence of torrefaction on morphology, thermal properties and composition of oil palm empty fruit bunch, mesocarp fiber and oil palm kernel shell. Recently, oil palm biomass residues were characterized to evaluate their potential for industrial chemicals (Onoja et al., 2017) and thermochemical conversion (Loh, 2017). Very recently, kenaf was evaluated as reinforcement material (Anuar et al., 2018), however it was noticed that mostly the studies were restricted to the properties of nanofiber (Zaini et al., 2013, Jonoobi et al., 2011, Aprilia et al., 2016, Zarina and Ahmad, 2015) and composites (Saba et al., 2016c, Saba et al., 2016a, Saba et al., 2016b, Devadas et al., 2018) derived from this biomass. Despite substantial work, the study focusing on physicochemical properties of raw biomass covering commonly available lignocellulosic residues in Malaysia including oil palm frond, oil palm trunk, oil palm empty fruit bunch, oil palm kernel shell, rice husk, rice straw and kenaf stalk, as well as their comparative evaluation in order to ascertain their potential for bioenergy and bio-based materials has not been done previously. This study would be useful because it can provide valuable insights on the suitability of these agricultural residues for successful downstream processing.

The fractionation of lignocellulosic biomass into its major components viz. cellulose, hemicelluloses and lignin is attractive, presenting incredibly vast potential for various energy and non-energy applications owing to unique physicochemical properties of these constituents (Mohtar et al., 2015). For example, sugars recovered from polysaccharides can be fermented to bioethanol (Lai and Idris, 2016) and abundance of functional groups such as phenolic, carboxylic as well as aliphatic hydroxyl groups in lignin provides possibility for fabricating green composites

(Albadarin et al., 2017). However, biomass processing in most cases being chemical and energy intensive is not sufficiently eco-friendly, together with problems due to equipment deterioration and biomass recovery adding to high processing costs (Serna et al., 2016, Watkins et al., 2015, Mohtar et al., 2015). Over the years, several processing approaches using solvents including sub- and supercritical water (Chan et al., 2017, Sivasangar et al., 2015, Chan et al., 2014, Chan et al., 2018, Mazaheri et al., 2013), hot compressed water (Goh et al., 2012, Goh et al., 2010), deep eutectic solvent (Tajuddin et al., 2019, Zulkefli et al., 2017) and ionic liquids (Financie et al., 2016, Ramli and Amin, 2014, Mohtar et al., 2015) have become an object of intense research for oil palm biomass residues, which account for over 90 % of the biomass generated from 5.85 million ha of oil palm plantation in Malaysia (MPOB, 2019).

The oil palm trunk and oil palm kernel shell are among the most underutilized agricultural residues, former is mostly left at plantations (Onoja et al., 2018), whilst shell is directly used as low-rank solid fuel with very limited efficiency (Yusoff, 2006). In view of explosive growth of oil palm industry, there is a strong need to identify more efficient and green routes as the global trend to utilize biomass waste continue to diversify from their traditional usages. In recent years, a series of processing approaches have been proposed for enhancing biochemical conversion yield from oil palm trunk, for example acid (Chin et al., 2011, Khamtib et al., 2011, Noparat et al., 2015), aqueous ammonia (Jung et al., 2011, Maryanto et al., 2018), sodium hydroxide (Lai and Idris, 2016, Prawitwong et al., 2012), sulfite (Noparat et al., 2017), hydrothermal (Eom et al., 2015), steam explosion (Punsuvon, 2013), organosolv (Rattanaporn et al., 2018), and lime (Sitthikitpanya et al., 2018). Similarly, many researchers have proposed different processing routes for oil palm kernel shell intended for the production of energy (Kim et al., 2010, Asadullah et al., 2014, Asadullah et al., 2013, Husain et al., 2002) and materials (Jumasiah et al., 2005, Abechi et al., 2013, Abechi et al., 2011, Salmah et al., 2012, Fono-Tamo et al., 2014).

Recently, high-pressure CO_2 has attracted increasing attention for sustainable processing of lignocellulosic biomass (Toscan et al., 2017). The supercritical carbondioxide (SC-CO_2) is essentially abundant, non-toxic, non-flammable, very volatile, cheap, recyclable and exhibit easy-reaching critical point (31.1 °C and 7.36 MPa) (Serna et al., 2016). The in-situ formation of carbonic acid promotes xylan removal from biomass and subsequent drastic release of pressure creates a physical "explosion effect" which results in a highly disrupted biomass heterostructure, improving its enzyme accessibility and bioconversion yields (Zhao et al., 2019). Although, SC-CO_2 technology has been investigated for the extraction and processing of palm oil (Birtigh et al., 1995, Davarnejad et al., 2008, Markom et al., 2001), however, considering substantial amount of oil palm biomass generated, its integration in oil palm-based biorefinery for other non-extractive applications has not yet been fully explored.

In addition to SC-CO_2, another useful solvent for biomass fractionation is tetrahydrofuran (THF) that has recently been identified as an innovative multifunctional solvent for biomass fractionation (Meng et al., 2018, Zhang et al., 2011). The use of THF as relatively non-toxic, easily recyclable, potentially sustainable and biodegradable solvent for biomass fractionation with catalytic qualities that promotes lignin recovery has gained attention from researchers worldwide (Nguyen et al., 2015, Meng et al., 2018, Cai et al., 2013, Fowles et al., 2013). The recovered lignin can be exploited as cheap feedstock for different applications, although it continues to remain a challenge till date, hence more studies are needed (Larrañeta et al., 2018, Wang et al., 2018b). Recently, researchers are interested in exploiting lignin as renewable feedstock in fabricating green materials (Yang et al., 2018b), in particular using nano-sized lignin (Yang et al., 2018a, Yang et al., 2015, Tian et al., 2017), nevertheless these studies are still in infancy. Earlier scientific work on nano-lignin involved hazardous chemicals, chemical functionalization steps and/or lengthier synthesis durations (Sameni et al., 2018, Yang et al., 2018, Qian et al., 2014a, Qian et al., 2014b). In contrast, the ability to facilely prepare nano-lignin directly from biomass as well as recycle and reuse THF seems economically promising with no adverse effect to the environment as compared to conventional methods (Zhang et al., 2010).

No work so far has been reported on the fractionation of oil palm trunk and oil palm kernel shell using SC-CO_2 and THF, respectively, for downstream application as bioenergy and bio-based material feedstock, respectively. The findings of this study would significantly contribute in promoting as well as commercializing innovative and green processing technologies in oil palm biomass-based biorefinery with distinct environmental and economic benefits, as well as for the overall sustainability in Malaysia.

1.2 Problem statement

Agricultural development on sustainable basis has led to a substantial rise in the quantity of lignocellulosic biomass residues in Malaysia. To deal with this biomass waste accumulation, open field disposal, compositing and mulching have been widely practised. However, these traditional ways of biomass waste recycling are inadequate and eco-unfriendly with no financial gains. Thus, there is a strong need to identify innovative routes for utilizing lignocellulosic biomass materials that are more efficient with minimum impact on environment.

Lignocellulosic biomass residues can be exploited as abundant, low cost and green raw materials for the production of bioenergy and bio-based materials because of their unique physicochemical characteristics, hence paving way towards the establishment of an integrated biorefinery. This approach seem viable and highly promising for building second-generation bio-based economy in Malaysia. However, the development of economically feasible integrated lignocellulose biorefinery is challenged by the highly heterogeneous, polymeric and multi-component structure of biomass, containing cellulose, hemicellulose, lignin along with inorganic components. As a result, there is a need for (i) characterization studies because different proportions of these components confer unique physicochemical properties to each lignocellulosic biomass, and (ii) various processing methods for deconstructing lignocellulosic biomass, as well as its refining into major components which can, in turn, be exploited for variety of downstream usages.

The most important and commonly available residues found in Malaysia's agricultural biomass reserves come from oil palm (oil palm frond, oil palm trunk, oil palm empty fruit bunch and oil palm kernel shell), paddy (rice husk and rice straw) and kenaf (kenaf stalk) crops, hence the study was planned to focus on these residues as the first phase. From the perspective of biomass utilization, fundamental studies on physicochemical characteristics of aforementioned agricultural residues as well as their comparative assessment to maximize their benefits are limited. This study would be important because it would help in ascertaining the candidacy and suitability of these biomass materials for successful downstream processing and prospective usages. Secondly, as the application of green chemistry has become increasingly vital in recent era, the choice of appopriate biomass processing presents a challenging task for future bio-economy. To reduce environmental footprints, the exploration of ecofriendly technologies using water, supercritical fluids, deep eutectic solvents, ionic liquids and bio-based solvents has been receiving increasing attention for oil palm residues for various applications. Thereupon, the study was designed to focus on the processing of two underutilized oil palm residues generated in massive quantity, i.e. oil palm trunk and oil palm kernel shell in the subsequent phases using simple, innovative and eco-friendly SC-CO_2 and THF-based methods, respectively, as no such work on these residues has been carried out before for application as a resource for bioenergy and bio-based materials, respectively.

1.3 Research questions

- Would the physicochemical characterization study be helpful in ascertaining the potential of commonly available agricultural residues in Malaysia including oil palm frond, oil palm trunk, oil palm empty fruit bunch, oil palm kernel shell, rice husk, rice straw and kenaf stalk for bioenergy and bio-based materials.
- Would it be possible to bring about significant changes in the morphology and other physicochemical properties of oil palm trunk using SC-CO_2 based experiment?
- Is SC-CO_2-based processing of oil palm trunk beneficial in improving the yield of glucose?
- What is the effect of operational parameters in SC-CO_2-based processing of oil palm trunk on glucose yield?
- Is SC-CO_2-based method simple, green and efficient compared to conventional processing using acid?
- Would it be possible to prepare nano-lignin directly from oil palm kernel shell using a facile and green route based on THF solvent?

- What is the effect of inclusion of nano-lignin from oil palm kernel shell as bioadditive on physicochemical properties of chitosan-based composite?

1.4 Objectives

The objectives of this work are enlisted below;

1. To evaluate the physicochemical properties of the lignocellulosic biomass residues commonly available in Malaysia, including oil palm frond (OPF), oil palm trunk (OPT), oil palm empty fruit bunch (EFB), oil palm kernel shell (PKS), rice husk (RH), rice straw (RS) and kenaf stalk (KF) in order to identify their potential for bioenergy and bio-based materials.
2. To study the processing of OPT based on the outcome of Objective 1 using SC-CO_2-based method, and investigate its physicochemical properties (composition, morphology, crystalinity and thermal stability) and application as bioenergy feedstock.
3. To study the processing of PKS based on the outcome of Objective 1 using THF-based method for preparing nanoparticles of polymer lignin (L_{NP}) and the physicochemical properties of L_{NP}, as well as application as bio-based material feedstock by fabricating a bionanocomposite.

1.5 Significance of the study

The lignocellulosic biomass offers remarkable opportunities for different applications because of their abundance as well as unique physical and chemical properties, hence paving way towards the establishment of lignocellulosic biomass-based integrated biorefinery. The lignocellulosic biomass residues generated in Malaysia, in particular, from oil palm industry offer remarkable opportunities in variety of industrial applications because they are generated in massive yields and most important feature is their unique physical and chemical properties which is essential for the establishment of biorefinery based on multiple feedstock. Nevertheless, there is still a long way to go in realizing the concept of integrated biorefinery system, an approach which is vital to address environmental issues, along with other benefits in terms of increased revenue because of the sustainable supply of final products which are competitive in the market and for overall sustainable development.

In view of phase 1 of this work, a total of seven agricultural residues were characterised and assessed for their suitability under the regime of biorefinery. This study would be a useful guideline in understanding the influence of various physicochemical factors related to biomass on their properties as well as in developing a zero-waste lignocellulosic biorefinery, especially with regard to oil palm industry, and will open up possibilities or new opportunities in various applications. Compared to previous such studies that were meant for a very specific role and are available in isolated forms in Malaysia, herein comparative evaluation of physicochemical properties of raw biomass covering commonly available agricultural residues is done to ascertain their potential for bioenergy and industrial materials. This study would be instrumental in designing novel biomass processing strategies, choice of appropriate technology as well as would promote cascade utilization of all biomass components in variety of potential applications.

The conventional methods of biomass processing are not sufficiently environmentally friendly because of intensive use of chemicals and energy, in addition to the high cost associated with equipment corrosion, among others. Although substantial amount of research has been done concerning biomass fractionation yet, the use of innovative, sustainable and eco-friendly methods based on SC-CO_2 and THF are limited in Malaysia. The work carried out in phase 2 and 3 of this dissertation demonstrates two approaches of biomass processing that are promising green routes for industrial gains with great potential to offer sustainability benefits. The SC-CO_2 processing of OPT carried out in second phase of this study is green because it avoids the use of toxic chemicals, solvent can be completely recycled with no residues and water consumption is very little as this process is a solid–gas reaction. Moreover, in comparison to the earlier scientific work on L_{NP} which involved hazardous chemicals, chemical functionalization steps and/or lengthier synthesis durations, the strategy followed in third phase of this study is simple and straightforward for the rapid formation of nano-lignin directly from PKS biomass.

1.6 Thesis outline

The organization of thesis is enlisted below;

- In **Chapter 1**, an overview of the thesis with background research has been discussed in the light of previous and recent research. Against aforesaid backdrop summarized in problem statement of this dissertation, objectives have been defined together with research questions and significance of this study.
- **Chapter 2** deals with a comprehensive literature review related to lignocellulosic biomass utilization in recent past, in particular, an account of the Malaysian biomass outlook has been included. The topics dealt with in this chapter take account of lignocellulosic biomass classification, composition, physicochemical properties and processing routes. Furthermore, under the regime of biorefinery, the utilization of lignocellulosic biomass residues from oil palm industry as renewable feedstock for bioenergy and bio-based materials has been summarized as well.

- **Chapter 3** provides the details on chemicals, standard methods, characterization studies and processing methods that were used in present work.
- **Chapter 4** embodies the original contribution of the thesis based on physicochemical characterization of a total of seven lignocellulosic biomass residues as renewable feedstocks to determine their suitability for biofuels and bio-based materials production. A range of analytical characterization techniques were used to determine proximate composition, CHNS/O analysis, calorific value and lignocellulosic content determination. In addition, thermal and spectroscopic analysis provided useful insight related to thermal, compositional and structural properties of selected biomass as well.
- In **Chapter 5,** based on initial screening of selected biomass residues, attention was later directed towards abundantly available field residue from oil palm plantation, i.e. OPT. Preliminary study on OPT revealed that it is an ideal feedstock for bioconversion because of its high cellulose content with low quantity of lignin, whilst, despite these benefits it is mostly left unharnessed at plantations. Herein, SC-CO_2-based pretreatment was applied to OPT and variations in physicochemical properties and their effect on the enzymatic hydrolysis yield from pretreated biomass as bioenergy feedstock was studied.
- In **Chapter 6**, based on initial screening of lignocellulosic biomass on the basis of physicochemical properties, PKS was identified as a rich source of lignin, and hence can be processed as renewable feedstock for lignin-based materials. Herein, processing of PKS was done using THF in acidic aqueous

system for the synthesis of nano-lignin directly from lignin rich PKS biomass. As-prepared L_{NP} were later used as bio-additive to fabricate a new bionanocomposite adsorbent for environmental remediation.

- Major findings of this dissertation have been summed up in **Chapter 7**, wherein certain recommendations for future direction have been suggested that would significantly contribute towards the establishment of economically viable lignocellulosic biomass-based integrated biorefinery in Malaysia.

CHAPTER 2

LITERATURE REVIEW

2.1 Potential of lignocellulosic biomass as a sustainable platform for the production of bioenergy and bio-based materials in a biorefinery

The conversion of lignocellulosic biomass to bioenergy and advanced materials has become an actively growing field of science and technology (Hassan et al., 2019). In view of extensive utilization of petroleum-derived raw materials, switching to sustainable materials is gaining increasing popularity among scientific community. Factors responsible for this trend are; depletion of fossil oils (unsustainable), fluctuating oil prices, and environmental concerns (non-biodegradable) (Mulimani, 2017, Adefarati and Bansal, 2019). The concept of biorefinery is dominating everywhere, and hence, many studies have been conducted for the production of biofuels and other chemicals using lignocellulosic biomass over three decades (Zhou et al., 2017, Torget et al., 2000, Scott et al., 1995).

According to the National Renewable Energy Laboratory (NREL), biorefinery can be defined as the facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass (de Farias Silva et al., 2019) as schematized in Figure 2.1, highlighting the conversion of various biomass components for energy and non-energy applications. In principle, a biorefinery essentially covers integrated process concepts that use biomass as a resource for the sustainable, preferably residue-free production of different products (construction materials, chemicals, composites, energy and/or fuels) (Harnisch and Urban, 2018).

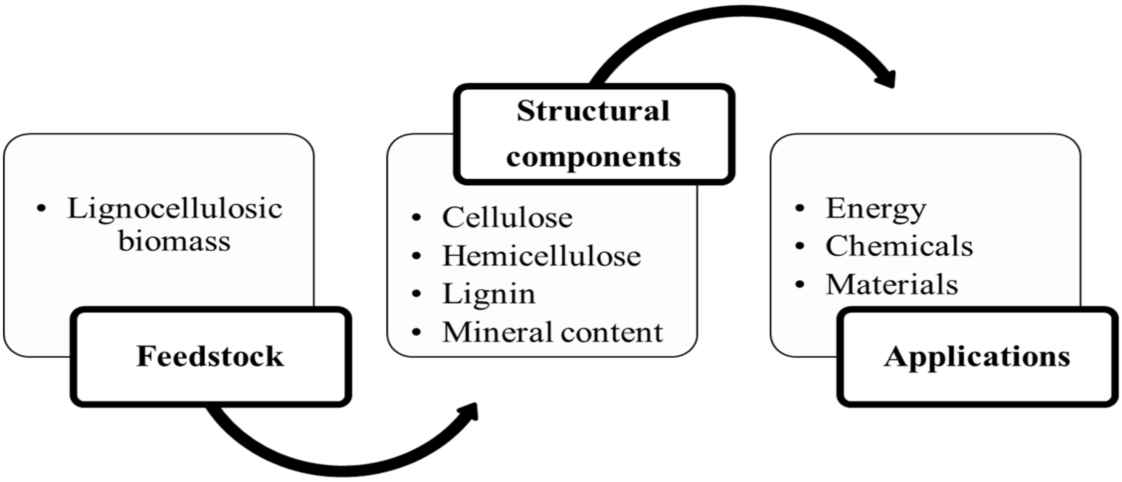

Figure 2.1. Lignocellulosic biomass-based biorefinery concept (Clark and Deswarte, 2008).

A number of platform chemicals can be derived from biomass via. variety of chemical routes in a biorefinery in a way similar to the processes undertaken in the petrochemical industry (Romero-Izquierdo et al., 2019). The prime aim of biorefineries is to reduce the reliance of modern society on environmentally unbenign and limited strategic-resource petroleum as a raw material.

Essentially, lignocellulosic biomass offers a multitude of potential applications in the form of variety of valuable byproducts towards the crossroads of food, feed and fuel. This is the reason why biomass processing has unequivocally become the focus of attention by vast majority of researchers in an attempt to satisfy the world demand for energy and materials, as well as to move away from traditional hierarchical approach of waste utilization (Mata et al., 2018).

The categories of lignocellulosic biomass feedstocks available for energy and non-energy applications fall into the following sectors: agriculture, forest, and industry as summed-up in Table 2.1.

Table 2.1 Lignocellulosic biomass feedstocks available for different purposes (Cai et al., 2017, Loy et al., 2018, Corley and Tinker, 2015).

Source	Category	Selected examples
Agriculture	Energy crops: oilseed, sugar and starch crops	Sunflower, sugarcane, wheat, corn
	Lignocellulosic energy crops	Herbaceous crops (switchgrass, miscanthus, reed)
	Crop residues	Corn stalk, cotton stalk, oil palm trunk, oil palm frond, rice straw, wheat straw
Forest	Dedicated	Short rotation plantation (willow, poplar, eucalyptus)
	By-products	Barks, wood blocks, wood chips and logs from thinning, wood chips from tops and branches
Industry	Agro-industrial residues	Rice husk, oil palm kernel shell, oil palm empty fruit bunches, sugarcane bagasse, corn cob
	Residues from wood industry	Waste wood from industries, sawdust
Other	Lignocellulosic waste material	Waste from parks and gardens (grass, pruning etc.)

Globally, agricultural residues are being generated in massive yields (billions of tons) on annual basis (Hassan et al., 2018) such as OPT and OPF obtained from oil palm plantation are the main field residues. Energy crops include starch crops (corn, wheat and barley), sugar crops (cane and beet), oilseed crops (soybean, sunflower, safflower), short rotation woody crops, herbaceous woody crops and grasses (Pacetti et al., 2015, Mitchell et al., 2016). In addition, the products from forestry activities such as trees, wood, shrubs and wood residues, logging residues, sawdust, bark, etc. also constitute a major source of lignocellulosic biomass (Caro et al., 2015) and have gathered attention for usage as energy source in bioenergy plant (Guilhermino et al., 2018). Besides, dedicated woody lignocellulosic biomass presents tremendous potential for energy generation, hence can also significantly contribute in future bio-economy (Chudy et al., 2019). Importantly, large quantity of agro-industrial biomass residues is accumulated and remain underutilized, for instance residues from oil palm industry such as EFB, palm kernel cake (PKC) and PKS in palm oil producing countries including Malaysia, Indonesia, Nigeria etc. In addition RH from paddy industry is generated in high yield, both in the country and worldwide (Maragkaki et al., 2018, Wang et al., 2018a). The main drive for exploiting lignocellulosic biomasses from different sectors enlisted in Table 2.1 as a source of raw materials in a biorefinery is that they are abundant, renewable and ecofriendly (Patade et al., 2018) together with signifying an important aspect of waste management (Pacioni et al., 2016).

Overall 10 % of the global primary energy supply was contributed by biomass alone by 2008, and further developments in this domain would trigger two to six-fold increase by 2050 (Ozturk et al., 2017). Transforming biomass into bio-based materials is another alternative to their transformation into energy. Globally, over 64 countries and sub-national governments have strongly supported bio-based products, biofuels in particular, whilst, the United States (US) and Brazil are considered as the major players. The European Union (EU) is also striving in this area (predominantly Germany), with an emphasis on biogas and biodiesel. In 2015, 190 establishments were recognized to be involved in the development of bio-based products (for example: biofuels, bioenergy, organic chemicals and intermediates, materials and composites) in Canada (Hassan et al., 2019, Rancourt Y, 2017).

In Malaysia, the tranformation of biomass to energy has already contributed in supporting the soaring demand for energy, however, compared to its European counterparts, it has been done on smaller scale (Ozturk et al., 2017). During the last two decades, Malaysia has experienced a radical rise in population as well as in economic development and, as a consequence, there has been an upsurge in demand for alternate source of energy and materials to fulfill its ever-increasing population and commercial energy demand. Every year, Malaysia produces more than 160 million tonnes of biomass including palm oil residues, paddy waste, coconut waste, sugarcane residues, forestry waste and municipal waste (Abdullah et al., 2019). Lignocellulosic biomass residues produced from agricultural activities have been identified as prospective resource of bioenergy and wide spectrum of bio-based products of industrial significance in Malaysia as discussed in Section 2.2.

2.2 Rationale for the choice of lignocellulosic biomass from agricultural residues in present study

Malaysia is tropical country located in the South East Asia region with rich biodiversity biomass potential. The climate in Malaysia is predominantly characterized by uniform temperature, high humidity and heavy rainfalls (Lau et al., 2016). Agricultural development on sustainable basis has led to a rise in the generation of lignocellulosic biomass residues in Malaysia. The utilization of these residues in a biorefinery can bring in distinctive benefits on environmental fronts due to waste recycling together with economic advantages because of sustainable supply of end products. However, the choice of biomass feedstock and appropriate processing technologies is a challenging task because of the intrinsic physicochemical properties of biomass residues. Therefore, physical and chemical characterization becomes very important step under the biorefinery concept.

The biomass resources were selected based on following factors; their availability in large volumes, so making large scale utilization economically beneficial (EFB, and OPF), contribution to environmental deterioration (RS and RH), potential for high value application (KF, EFB, RH and OPT), economic mobilization in rural regions (KF and RS). According to the Malaysian Industry Group for High Technology (MIGHT), these residues being major sources of biomass in Malaysia are also covered under strategic action plan 2020 for developing and promoting stakeholders in implementing sustainable production through participation in the Malaysian biomass industry (MIGHT, 2013). These agricultural residues were the focus of phase 1 of this work and are discussed in sub-sections 2.2.1 to 2.2.3, under the category of oil palm, paddy and kenaf industry.

2.2.1 Oil palm industry

The oil palm (*Elaeis guineensis*), a multipurpose and perennial plant belonging to *Palmae* family has been an object of commerce since long. This is in fact, in large measure, owing to the versatility of the products obtained after processing (Gray, 2018). It is an important cash crop in over 45 countries across Asia Africa and America. The oil palm has extended history of utilization by human for different purposes for as long as 5000 years (Coursey et al., 1984). The oil palm was found as early as 3000 B.C and archeological evidences indicate that it was traded to different places. It was brought to ancient Egypt by Arab traders and was considered by pharaohs to be a sacred food (Ndon, 2006, Fife, 2007). There are various fossil, historical, and linguistic evidences suggesting that oil palm has its origin in Africa (Hartley, 1967). It has been proposed that oil palm was brought to Africa in pre-Colombian times (Corley and Tinker, 2008). From Gulf of Guinea (Africa), center of origin, the oil palm exists as wild, semi-wild and cultivated plant in developing regions with comparable weather conditions mainly, South east Asian countries, i.e., Indonesia and Malaysia, Central America, few countries in Latin America including Brazil, Honduras, and Ecuador and Oceania (Jacquemard, 1998, Corley and Tinker, 2008). The oil palm belt is extended across Sierra Leone, Ivory Coast, Ghana, Togol, Benin, Cameroons, Congo and Nigeria in Africa. On the other hand, in South East Asia which is the largest producer of oil palm, it is mainly distributed in Sabah and Sarawak in Malaysia. In Indonesia, oil palm is largely cultivated in Sumatra, Kalimantan, Sulawesi and West Papua where further expansion to other areas such as Siberut, Halmahera and Yamdena is in progress. Further, according to the reported data by M. Colchester and S. Chao, Philippines where the oil palm plantation is concentrated in Mindanao, the provinces of Bohol in the Visayas and Palawan in Luzon, may soon emerge as a key producer in the palm oil industry of South East Asia (Colchester, 2011). In the early 19th century, the attempt of planting oil palm on experimental basis in West and West Central Africa by Europeans failed (Martin, 2006b).

As far as early plantation on the land of South East Asia is concerned, so a Belgium engineer, Adrien Hallet, working in Sumatra observed that owing to richer soil, rainfall and sunlight, oil palm grew better thus resulting in richer fruit as compared to that found in Africa in 1905. The oil palm was originally planted in Malaya by Henri Fauconnier, a friend of Hallet in 1910s. The oil palm was commercially planted in South East Asia in 1948 by growing the seedlings brought from West Africa in Java (Martin, 2006a). The palm industry flourished vastly in South East Asia due to maximum yield and low potential risk involved. In addition, another key factor in inclination towards palm oil industry was to reduce reliance on rubber industry (Kiple, 2000). On the other hand, the palm genera found in America is believed to have South American origin but the Portuguese terms describing oil palm have African origin. Further, the first commercial plantation of palm oil in Latin America took place in Guatemala in 1940 assisted by United Fruit Company although initial plantation was carried out in 1927 in Honduras, now one of the largest producers in Latin America, which turned out to be unsuccessful by then (Hartley, 1967, Corley and Tinker, 2008).

The palm oil industry provides a major share of available biomass in Malaysia. In Malaysia, the supply of oil palm biomass is anticipated to increase to around 100 million dry tonnes of solid biomass per annum from the palm oil sector (MITI, 2019). The oil palm residues are classified into two, namely by-products obtained from plantations sites (field residues) and from palm oil milling. The former includes two main by-products: OPT and OPF, while oil palm EFB, PKC, palm oil mill effluents (POME), pressed palm fiber (PPF), and PKS are obtained from the later (Agensi Inovasi Malaysia, 2013). The oil palm biomass is constantly generated in large quantities annually with a small fraction being converted into energy and other value-added materials, while still a large proportion remains underutilized (Onoja et al., 2018). Therefore, oil palm biomasses such as OPF, OPT, EFB and PKS were selected for the comprehensive investigation due to high yields and diversity of these residues in order to assess their potential to produce ecofriendly materials under the regime of biorefinery for circular green economy.

2.2.2 Paddy industry

Rice is mostly consumed in Asia as a staple food, accounting for over 80 % of the world's rice consumption particularly in the Southeast Asia as hub of the world's rice economy as highlighted in a report by Khazanah Research Institute (KRI, 2019). Being a major consumer of rice, paddy production in Malaysia has been ranked as an important agricultural output. According to Food and Agriculture Organization (FAO) of the United Nations, 2.84 Mt of rice was produced in 2017 in Malaysia (FAO, 2018). Paddy production generates two kinds of residues, i.e. RS which refers to the stalk of the rice plant that is considered as waste material left in the field after harvesting of the rice grain. While, RH is the outer layer of a rice grain which is removed from the rice seed during milling process (Pode, 2016). The RH constitutes 20 % of the total rice produced, whilst remaining 80 % of the weight is collected as rice grain. For every kilogram of rice grain harvested, 1 to 1.5 kg of paddy straw is generated. The paddy waste is estimated to reach 7 Mt per year by 2020 in Malaysia due to technological breakthroughs in agricultural sector (Shafie, 2015), with the consequence of waste management problems especially in the developing countries.

2.2.3 Kenaf industry

From bioenergy perspective, little is known about kenaf plant, a short day annual non-food crop grown commercially in many places worldwide particularly in Southern Asia (Kargarzadeh et al., 2012). The bark, pith and branchless stalk are the residues of the plant that can be of great use as a feedstocks in biorefinery applications (Meryemoğlu et al., 2014, Krull and Inglett, 1980). This plant is profitable as feed crop for its fiber content, medicinal usage, production of twine, rope, paper and others. Essentially, it offers a multitude of potential applications, giving, a part of fiber, variety of valuable byproducts towards the crossroads of food, feed and fuel (Kipriotis et al., 2015). In Malaysia, it was first introduced as early as 1970's, recognized as potential alternative fibrous materials of board products, such as fiber board and particle board under the Seventh Malaysian Plan. Further, research and future development of kenaf-based industry in the states of Terengganu, Pahang and Kelantan under the Ninth Malaysia Plan (2006-2010) led to an explosive rise in kenaf plantations and kenaf seed production since 2006 (Cheng et al., 2016, Saba et al., 2015). According to the National Kenaf and Tobacco Board (NKTB) report, the crop area in 2017 was 1,408 h with the total yield of kenaf seed and kenaf dried stem of 19.212 t/h and 10.367 t/h, respectively (NKTB, 2018).

According to the Ministry of Primary Industry (MPI), kenaf production is estimated to increase to 10,000 h through increased plant area and productivity with great potential in construction industry as well as in promoting green technology (MPI, 2019). Despite ecofriendly features such as short plantation cycle, flexibility to environmental conditions and relatively lower need for pesticides and herbicides compared to other lignocellulosic biomasses as well as being economically feasible feedstock, kenaf has rarely been exploited (Saba et al., 2015). This crop has found profound uses in automotive, oil and gas industry, however more research is needed for ASEAN countries in order to capitalize on the sustainability benefits of this plant (Thomas, 2019). The stalk being a major portion of the kenaf plant was selected for first phase of this work. Some aspects of the selected agricultural residues along with their digital photographs have been provided in Table 2.2.