Potassium Removal from Palm Empty Fruit Bunch for Slagging and Fouling Reduction

Chhenglong Tan

**A Thesis Submitted in Fulfillment of the Requirements for the Degree
of Master of Engineering in Environmental Engineering
Prince of Songkla University
2018**

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ABSTRACT

Gigantic waste from palm oil mills known as palm empty fruit bunch (EFB) is useful biomass waste residue for combustion power generation. Barrier for utilizing it as the solid fuel lies in its high potassium (K) composition. In this study, hydrothermal treatment at 60 and 120 ℃ as well as ambient temperature treatment at 28-30 ℃ (considered as soaking set) for 30, 60, and 120 min under 50, 75, and 100 g/L (EFB total solids to distilled water ratio) were applied aiming to remove K, and at the same time to reduce slagging index (SI) and fouling index (FI) in EFB boiler. Experimental results proved that increasing treatment temperature and detention time while lowering total solids concentration (TS) for hydrothermal and ambient temperature treatments promoted higher K removal and slagging and fouling reduction, respectively. Linear regression evidenced that there is the reduction in both indices when K removes through inverse correlation with sufficient coefficient R^2 of 0.76, 0.98, and 0.87 for remaining K vs. SI and of 0.85, 0.97, and 0.84 for remaining K vs. FI from treatments under 50, 75, and 100 g/L TS, successively. In comparison with the K of 20,467 mg/kg in raw EFB (without any treatment), highest K removal with the value of 90.7 ± 0.10 % (1,910 ± 14.4 mg/kg remaining), 88.8 ± 1.00 % (2,301 ± 210 mg/kg remaining), and 87.9 ± 0.0 % (2,468 ± 173 mg/kg remaining) were obtained at highest temperature of 120 ℃ for longest detention time of 120 min under the three TS, respectively. In addition, the regression model expressed a

good fit to the data and able to describe the relative interaction of the three independent variables on K removal with the significant difference of $p < 0.0001$ and the high determination of coefficient R^2 of 0.89. According to the mass balance, which is the research closure, showed that EFB was reduced in its TS amount from 419 to 305 kg/ton EFBwet (~ 27.2 % loss) at the end of process flows; promoting the removal and reduction of some adverse parameters like K, SI, and FI as the good findings for better EFB fuel quality and combustion power plant.

ACKNOWLEDGEMENTS

CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Al	Aluminium
Al_2O_3	Aluminium Oxide
Ba	Barium
Be	Beryllium
^oC	Degree Celsius
C	Carbon
C/H	Carbon to Hydrogen Ratio
C/O	Carbon to Oxygen Ratio
CV	Coefficient of Variance
Ca	Calcium
CaO	Calcium Oxide
CF	Core Fiber
CH_4	Methane
Cl	Chloride
CO_2	Carbon Dioxide
COD	Chemical Oxygen Demand
Cs	Caesium
EDX	Energy Dispersive X-ray
EFB	Palm Empty Fruit Bunch
Fe	Iron
Fe_2O_3	Iron (III) Oxide
FI	Fouling Index
Fr	Francium
g^*	Gaseous
g	Gram
g/L	Gram per Liter
H	Hydrogen

H/C	Hydrogen to Carbon Ratio
HCl	Hydrochloric Acid
HHV	Higher Heating Value
H_2O	Water
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
K	Potassium
K^+	Potassium Ion
KCO_3	Potassium Carbonate
KCl	Potassium Chloride
$KHSO_4$	Potassium Bisulfate
K_2O	Potassium Oxide
KOH	Potassium Hydroxide
K_2S_2O	Potassium Persulfate
K_2SO_4	Potassium Sulfate
l	Liquid
L	Liter
Li	Lithium
MC	Moisture Content
Mg	Magnesium
MgO	Magnesium Oxide
min	Minute
Mn	Manganese
μm	Micrometer
N	Nitrogen
NO_x	Refers to Nitrogen Monoxide and Nitrogen Dioxide
Na	Sodium
Na_2O	Sodium Oxide
O	Oxygen
O/C	Oxygen to Carbon Ratio

OH^-	Hydroxide Ion
P	Phosphorus
Ra	Radium
Rb	Rubidium
Rd	Ramp-down Time
rpm	Revolutions per Minute
RSM	Response Surface Method
Ru	Ramp-up Time
s	Solid
S	Sulfur
SO_x	Refers to Sulfur and Oxygen Containing Compounds
SO_2	Sulfur Dioxide
SO_3	Sulfur Trioxide
SEM	Scanning Electron Microscope
SI	Slagging Index
Si	Silicon
SiO_2	Silicium Oxide
Sr	Strontium
THB	Thai Baht
Ti	Titanium
TiO_2	Titanium Dioxide
TS	Total Solids
VS	Volatile Solids
wt	Weight
XRF	X-ray Fluorescence Spectrometry

CHAPTER 1

INTRODUCTION

1.1. Background and problem statement

For decades, increment of the oil palm plantation has been annually risen in Thailand due to the needs of its derived palm oil products for local consumption and exportation. A number of literatures reported that palm oil is the most beneficial oil compared to other bio-oils; i.e. soybean, peanut, sunflower, and rapeseed oil because of its versatility in use as an important component in chemical, food and biodiesel industries (Basiron & Chan, 2004; Colchester et al., 2011; Schmidt, 2015). This truth pushes massive growth of this economic crop and at the same time generates extreme amount of palm empty fruit bunch (EFB) as biomass waste. This EFB biomass produced in all standard palm oil mills is accounted for 24-29 % of all byproducts (Hengniran, 2010; Lecksiwilai et al., 2016; Pleanjai et al., 2007). The work on oil palm biomass-related reported that EFB in the quantity about 1.5 tons of hectare/year is produced from palm fresh fruit bunch (Abd Majid et al., 2012; Md Yunos et al., 2017a).

Although EFB could be converted by various methods such as bio-conversion and thermo-chemical, the yield of biofuels are still limited due to its recalcitrant nature of the EFB fiber. Putting it back to the plantation adds insufficient space and releases bad odor and greenhouse gases during the decomposition (Alam et al., 2007). EFB can directly be used as fuel in combustion system to convert to energy. Yet still, the presence of the high potassium (K) concentration, which is known as the major inorganic or alkaline element, in fiber itself makes it difficult for combustion application by developing combustion-related problems through the formation of slack in the

grate floor and heat exchange surface in combustion chamber (Mohammed et al., 2012; Obernberger & Thek, 2004; Saritpongteeraka et al., 2015).

Other literatures on biomasses as well as EFB also cited that some abundant minerals and inorganics (Cl, Fe, Ca, Mg, Na, K, Si, Al, and Ti) create ash-forming components and oxide compounds (e.g. Fe_2O_3, CaO, MgO, Na_2O, K_2O, SiO_2, Al_2O_3, TiO_2) during combustion that affect the heat transfer in boiler slagging index (SI) and fouling index (FI) (Abdullah & Sulaiman, 2013; Madhiyanon et al., 2012; Nutalapati et al., 2007; Pronobis, 2005; Zhu et al., 2014). The low melting point of these compounds at low temperatures in combustion power plant produces slacks accumulating in the boilers causing ash meltdown, frequent shutdowns, loss of efficiency, and raises the cost of maintenance for the furnace (ISTA, 1999; Theis et al., 2006).

SI and FI can be defined by different ash deposits accumulated in combustion system or boiler (Hare et al., 2010) at typical burning temperatures of the furnace 700-900 °C (Khan et al., 2009; Konsomboon et al., 2011; Rahbari, 2011). However, SI term is a highly viscous state of ash deposit forming a liquid layer, which is particularly a molten deposit of ash particles and when it contacts the boiler tube surface then it tends to solidify (sticky particle) due to the lower temperature of the boiler tube (Benson et al., 1993; Couch, 1994). K and SiO_2 reaction resulted in deposits (fused glassy and heavily sintered), which are SI. Clearly, potassium chlorides and sulfates were condensed on furnace walls, while convection tubes became coated with alkali chlorides, carbonates and sulfates mixed with silica, alumina and complex silicates (Mettanant et al., 2009; Miles et al., 1995; Turn et al., 1998). FI is the undesired deposits formation on surfaces of heat transfer, which increase the resistance to fluid flow, resulting in higher pressure drop and reduced heat transfer and it happens when the inorganic elements stick on the surfaces of the combustion unit. FI generally causes the performance of heat exchangers to degrade overtime. Like other deposit formations discussed some alkaline metals like K, Cl, Si and S are majorly

associated with FI problems, with also Ca, Mg, and P contributing (Al, 2012; Benson et al., 1993; Couch, 1994; Rahbari, 2011).

The reduction of alkaline metals and compounds in biomass would reduce the both indices, and it means to save the heating equipment for longer periods and the maintenance costs (Khan et al., 2009) since adverse effects from combusting biomass can have impacts on all parts in the combustion processes such as furnace, heat exchanger, turbines, emission control devices, and other equipment. At some power plants, the soot blower with the nozzle and ash behavior prediction tool (AshPro^{SM}) are being used in order to clean the boiler heated surface during operation with the blowing medium of water or steam and predict SI-FI situation (Hare et al., 2010). Thus, pretreatment on biomass prior for combustion is very necessary to overcome limitations above and it can improve biomass (Liu et al., 2013; Novianti et al., 2015; Reza et al., 2013).

Researchers have been finding optimized technologies like mineral additives (e.g. kaolin), chemical, biological, and physical pretreatments (e.g. hydrothermal) on biomasses fuels to solve and prevent the issues mentioned causing by these indices. But hydrothermal treatment seems one of the most interesting pretreatments since it produces higher energy density biomass through inorganics removal (e.g. particular K removal) and other important by-products (e.g. sugars, biogas) (Hoekman et al., 2011; Kim et al., 2015; Liu et al., 2013; Novianti et al., 2015; Nurfahmi et al., 2016; Shamsudin et al., 2012).

Hydrothermal treatment is a possible method to improve the EFB biomass into a more hydrophobic, more stable, and more lignin containing feedstock (Byrappa & Adschiri, 2007; Novianti et al., 2016). Hydrothermal treatment is earlier clarified that it influences not only on the changes of EFB structure, the better thermochemical conversion, the removal of oil, but also on the K removal (Md Yunos et al., 2017a; Novianti et al., 2015; Reza et al., 2013). Since EFB structural cell will be weakened by high temperature and K ion could hypothetically dissolve and remove with water. Hydrothermal treatment process

could facilitate this reaction (K^+ (s) + H_2O (l) => KOH (l) + $2H^+$) (Prawisudha et al., 2014; Sun et al., 2013) at various degrees for different conditions. In some studies, Hydrothermal treatment of EFB had been done at temperatures above 100 °C; and as the results, up to 77 % K removal was found; and it was reported that SI and FI would reduce as well (Prawisudha et al., 2014). Nevertheless, those studied temperatures and EFB material are higher (150, 175, and 200 °C) and different (fresh EFB) compared to this work. Additionally, this study will be calculating SI and FI in value and comparing to the standard limits as the either potential evaluation or proof on these indices (Zhu et al., 2014). The use of temperatures in hydrothermal treatment are still complicated as well as varied based on the research purposes. However, using of the temperature at lower than or equal to 100 °C could save energy and more practical (Kumar et al., 2009; Nurdiawati et al., 2015b).

This study aims to evaluate the effects of 3 independent parameters including total solids concentration of EFB to distilled water ratio (g/L), temperature (°C), and detention time (min) on performance of particular potassium (K) removal and at the same time on SI and FI reduction. It focused on potassium removal determination in solid EFB part (treated solid EFB sample) after the treatment. Treated solid EFB sample was also generated to EFB ash at 850 °C for 15 min by tube furnace prior to oxide-forming components analysis, SI and FI were then calculated. Quantitative K by energy dispersive X-ray (EDX), potential total oil recovery, and mass balance were also reported.

1.2. Objectives

The main objectives of the research are:

1). To investigate the effects of hydrothermal treatment at different total solids, temperatures, and detention times on potassium (K) removal from EFB.

2). To investigate slagging index (SI) and fouling index (FI) from EFB.

1.3. Benefits expected

There are 3 major benefits expected from this work:

1). Using hydrothermal treatment to treat EFB biomass was expecting to sufficiently remove the particular K substance from its fiber in order to get high EFB fuel quality. Once treated EFB being used as fuel, it would be expecting to reduce in SI and FI as well.

2). The used conditions (total solids, temperatures, and detention times) in this work as lab-scale treatment would expect to be the useful guideline for treatment method improvement as well as for the industrial scale of power plant factory.

3). Once the treating process worked well at the power plant, it would be economical in terms of the EFB wastes management, smooth process flow, and the maintenance.

1.4. Scope of study

EFB with 2-5 cm size was the studied raw material. It was well dried and prepared for proximate analysis, ultimate analysis, inorganic elements, elemental compositions, chemical compounds, and others as its raw characteristics. Main hydrothermal treatment was held using lab-scale autoclave facility under 3 independent variables, including total solids concentration (50,

75, and 100 g/L), temperatures (60 and 120 $^{\circ}$C), and detention times (30, 60, and 120 min). Each treatment was run in 3 replicates in order to affirm the data accuracy. The important dependent parameters, including remaining K content using inductively coupled plasma optical emission spectrometry (ICP-OES), K removal (by comparing between K in raw and treated EFB), SI and FI were analysed at the end of experiment by XRF. Potassium removal efficiency (%) was plotted against SI (% dry wt) and FI (% dry wt) in order to prove the effectiveness of treatments on K removal and SI and FI reduction. The full factorial design of the relationship of key parameters namely total solids (g/L), temperature ($^{\circ}$C), and detention time (min) as the 3 response factors with K removal (%) as an interested response of the regression model was also done.

CHAPTER 2

LITERATURE REVIEW

2.1. Oil palm plantation

The growth of oil palm crop has been increasing massively in the world since palm oil extracted from this plant is a basic ingredient of processed foods that we normally and commonly eat. Also, palm oil is the oil which uses widely in household cleaners and cosmetics (Colchester et al., 2011). In the Southern of Thailand, it is the second most traded economic crops after rubber. The largest growing areas of oil palm are Indonesia, Malaysia, and Thailand. Approximately, palm oil production output almost 20 million tons derives from 8 million hectares of total plantation in Indonesia. Nowadays, the percentage of agricultural land of oil palm plantations in Malaysia is up to 70 % or it takes the total area of 12 % (Jinn et al., 2015; Novianti et al., 2014; Sung et al., 2010).

Table 2.1 Planted area, productivity, and oil palm yield in kg per rai in Thailand.

Province	Planted area (rai)	Productivity (ton)	Yield per rai (kg)
Trat	50,535	133,478	2,641
Chon Buri	93,950	279,156	2,971
Prachuap Khiri Khan	108,982	299,318	2,746
Chumphon	762,190	2,332,397	3,060
Ranong	68,359	214,889	3,144
Surat Thani	982,440	3,282,165	3,341
Pang Nga	160,350	502,268	3,132
Krabi	950,447	3,320,117	3,493
Trang	149,396	461,505	3,089
Nakhon Si Thammarat	278,555	808,682	2,903
Satun	98,966	220,233	2,225
North	29,701	31,405	1,057
North east	64,610	90,210	1,396
Central region	381,201	1,004,399	2,635
Southern	3,548,308	11,346,491	3,198

Source: (OAE, 2017).

According to agricultural trends, southern provinces of Thailand is well-known area with oil palm plantations. It is about 90 % of the total area planting this kind of plant (Colchester et al., 2011). Table 2.1 shows some data of some planted locations or some important areas of oil palm and its average annual yields (OAE, 2017).
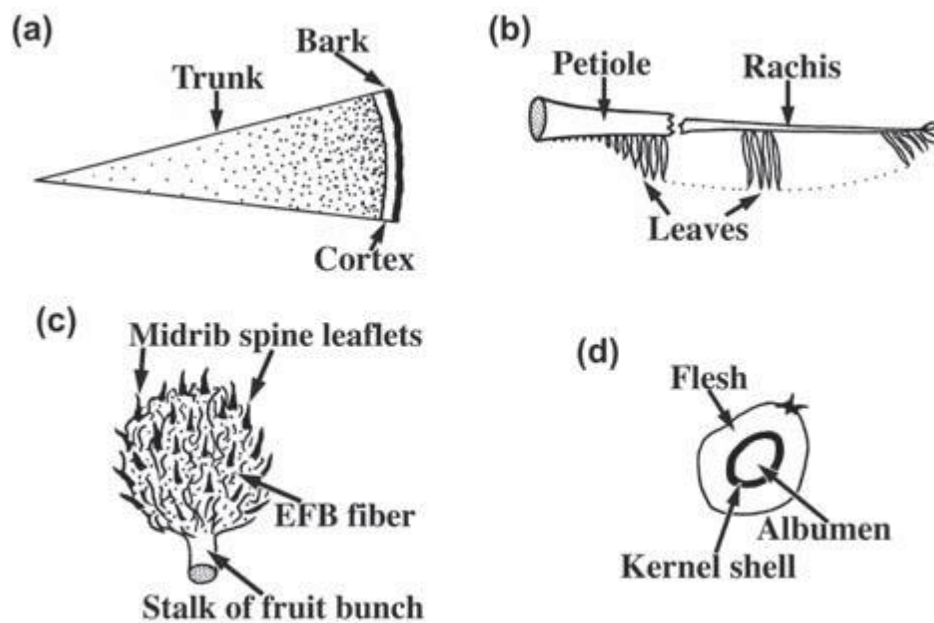
Fig. 2.1 The oil palm parts (Kawamura et al., 2014).

There are various solid biomass residues from oil palm crops and oil mill plant such as empty fruit bunch, palm press fibre, palm kernel cake, palm kernel shell and palm oil mill effluent. Additionally, there is in huge amount or quantity of palm oil mill effluent (POME), which is the non-solid biomass discharged from washing and sterilization of the palm fruits (Jinn et al., 2015). Fresh EFB are used in the process of mills and they generate numerous quantities of solid wastes which are biomass residues including shell of 5 %, mesocarp fiber of 12 %, and EFB of 23 % from every ton of fresh EFB (Chaikitkaew et al., 2015). It is reported that biomass residues after oil extraction process is 90 % while the oil rate is only 10% (Basiron & Chan, 2004). Fig. 2.1 presents the parts

of oil palm; which (a) is the cross section of trunk, (b) frond, (c) empty fruit bunch, and (d) the cross section of fruit (Kawamura et al., 2014).

2.2. Generality of plants lignocellulosic structure

Review on lignocellulosic materials affirmed the huge amount of available lignocellulosic residues, agricultural wastes, and wood wastes, i.e. as shown in Fig. 2.2 (Singh et al., 2014). Plants consist of cellulose, hemicellulose, and lignin on their cell walls as shown in Fig. 2.3 (Song et al., 2017). These three chemical compositions are the particular natural lignocellulosic structures. Cellulose of 40–50%, hemicellulose of 10– 30%, and lignin of 20–30% of lignin are found in plants; and these components are different according to types of materials (Singh et al., 2014).

| Wood pellet | Wood chips | Rice straw | Wheat straw |
| Palm waste | Sugarcane | Bio wastes | Short rotation coppice |
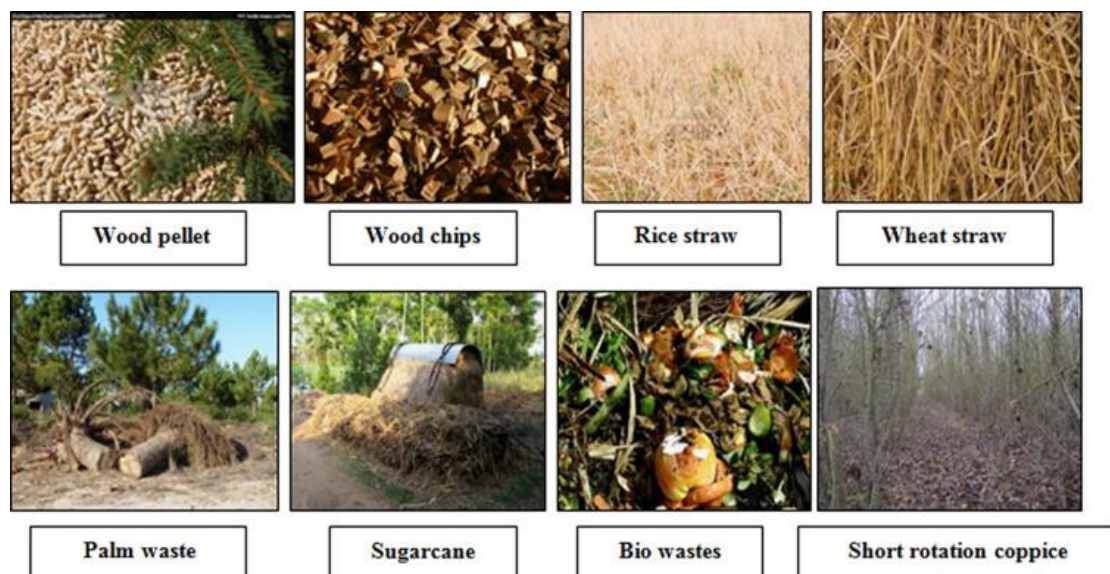
Fig. 2.2 Examples of some lignocellulosic agricultural waste and crop (Singh et al., 2014).
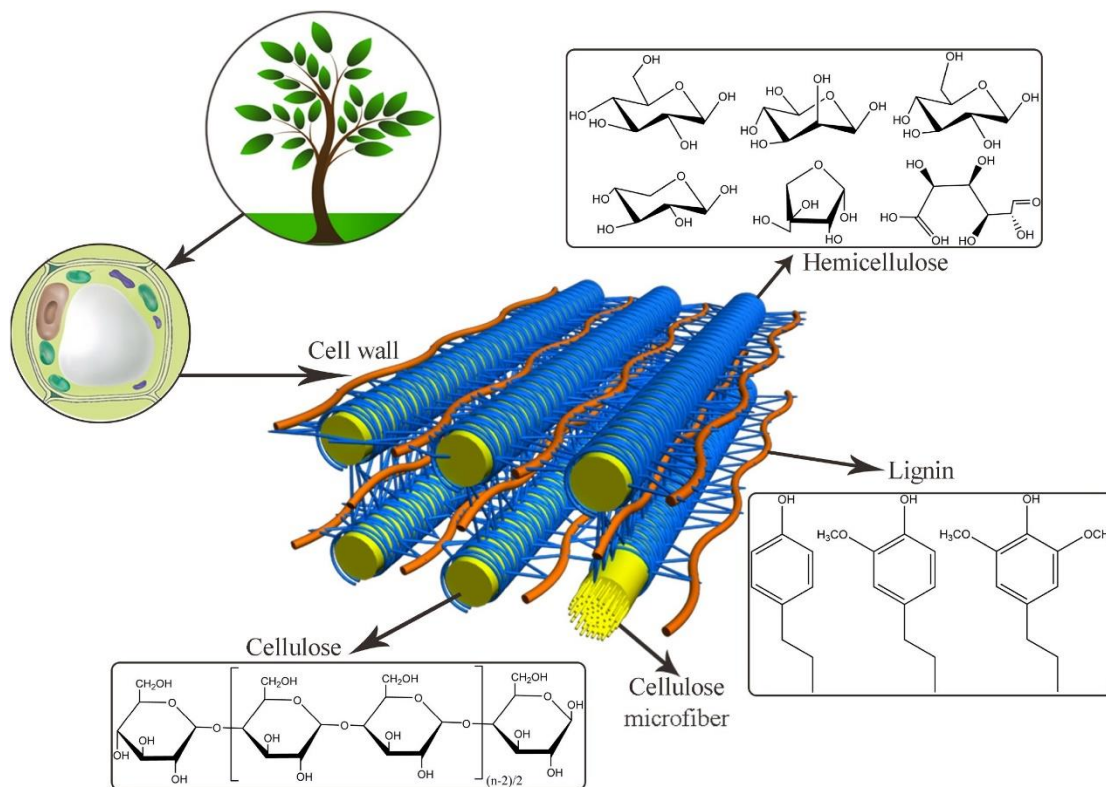
Fig. 2.3 Lignocellulosic structure (Song et al., 2017).

Cellulose is widespread in marine algae, bacteria, biomass, and other higher plants. It is the most abundant renewable organic resource with regular arrangement and gather into bundles; also cellulose is the framework of cell wall determination (Chen, 2014). Specific cellulose structure, a beta (1–4) linked chain of glucose molecules, helps a tightly packed and highly crystalline of polymer chains that is water insoluble and resistant to depolymerisation (Mosier et al., 2005). Hemicellulose is another major chemical composition in plant fiber materials. In opposite to cellulose, it is a copolymer composed of different amounts of several saccharide or sugar molecules (pentose group, hexose group, uronic acid, and others). Hemicellulose is commonly attached to the micro-fibrils surface, interweave with each other, and form dense amorphous network structure in the biomass internal structure. Differently from cellulose and hemicellulose, lignin is composed of three major phenolics (p-coumaryl alcohol,

coniferyl alcohol, and sinapyl alcohol) and restrains in the tissue of wood that hardens cell wall with its intertexture network formation (Österberg & Valle-Delgado, 2017; Song et al., 2017).

2.3. Palm empty fruit bunch

Palm empty fruit bunch (EFB) is a by-product after the mills processing. It has been recognized as a most potential biomass for energy production in Thailand. Fig. 2.4 is an example of fresh and palm empty fruit bunches (Khor et al., 2009). The EFB is disposed after the palm fruits are taken apart and its gigantic amount is considered as an important renewable resource when fully utilized. It has a very fibrous texture and it is in wet condition at the raw state after processing. In addition, lignocellulose (combination of cellulose, hemicellulose, and lignin) from 30 to 35%, residue oil from 1 to 3% and moisture content of 60% are remained after oil mill processing (Abdullah et al., 2011; May Jinn et al., 2015; Gunawan et al., 2009).

Fig. 2.4 Example of fresh and palm empty fruit bunches (Khor et al., 2009).

Geng (2013) reported that EFB is majorly rich biomass, one third, if compare to other biomasses from oil palm and it is the most interesting biomass for the production of bio-chemical, wood-related-products and energy. In the near future, EFB will be the main portfolio for sustainable growth and

development of materials for industry, energy, and also for bio-chemical. Table 2.2 shows EFB properties from reviews. The main point about table 2.2 is the high amount of K that might get from the use of nutrients, NPK, and this high amount of K may cause bad effect to combustion system such as SI and FI.

Palm plantation expansion in Thailand causes large volume of EFB which is residual or solid wastes. For instance, it is counted that the amount of EFB residues had increased at 4.85 million tons in 2012. Noticeably, EFB contains content of high carbon in a lignocellulosic form which comprises cellulose of 39.1 ± 0.8 %, hemicellulose of 22.0 ± 1.2 %, and lignin of 23.0 ± 0.7 % (OAE, 2012; Saritpongteeraka et al., 2014) However, these components can be varied depended on its biomass structure and analysis. Although, EFB has been satisfied as the significant biomass for further uses and production of renewable energy. It still leaves bad effects in combusting EFB boilers (corrosion, SI, and FI) since it contains abundant alkaline metals (Li, Na, Ra, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, and particularly K) (Konsomboon et al., 2011).

Table 2.2 Characteristics of palm empty fruit bunch.

Parameter	Value
Proximate analysis (wt% dry basis)	
MC[1,2]	38.4-60.0
Volatile matters[3,4,5,6]	67.5-79.8
Fixed carbon[4,6,5,3]	10.5-27.9
Ash[5,3,6,4]	4.30-13.7
Nutrients and elemental analysis (wt% dry basis)	
Carbon (C)[3,6,5,4]	40.7-53.2
Hydrogen (H)[3,6,4,5]	5.40-6.30
Oxygen (O)[5,4,6,3]	36.7-47.8
Nitrogen (N)[3,6,5,4]	0.30-1.00
Sulphur (S)[6,5,4,3]	0.10-1.20
Potassium (K)[5,7]	2.20-2.40
Phosphorus (P)[7]	0.60
Calcium (Ca)[7]	0.60
Iron (Fe)[7]	1.00
Magnesium (Mg)[7]	0.60
C:N ratio[7,1]	58.9-136
Chemical components (wt% dry basis)	
Cellulose[8,7,5]	38.3-59.7
Hemicellulose[8,5,7]	18.9-28.8
Lignin[7,5,8]	17.1-22.1
Other characteristics (MJ/kg dry basis)	
Higher heating value[3,5,9]	19.0-19.4
Lower heating value[10,5]	16.8-17.2

Source: (Madhiyanon et al., 2012)[1], (Rozhan et al., 2016)[2], (DEDE, 2010)[3], (Ruengvilairat, 2012)[4], (Geng, 2013)[5], (Konsomboon et al., 2011)[6], (Baharuddin et al., 2009)[7], (Kong et al., 2014)[8], (Abdullah et al., 2011)[9], and (Novianti et al., 2015)[10].

2.4. Biomass fuels benefits and inconveniences

Biomass fuels are unquestionably utilising for energy generation. Back in the previous decades, there were still many debates if biomass fuel is sustainable and useful. Returning back to today, researchers have been trying to find biomass energy feasibility. As the results, biomass materials really provide notable and numerous benefits since they take over fossils fuels; which it reduces greenhouse gases emission. A number of literature reported that there are two potential biomass resources including the wastes and purpose-grown-energy crops. Forestry residues, wood residues, sewage, tropical crop wastes, temperate crop wastes municipal solid wastes, and animal wastes are group of the wastes. For more, energy crops contain agricultural (i.e., oil palm residues, rice husks, and sugarcane bagasse) and wood crops (Saidur et al., 2011b). Table 2.3 describes the benefits and inconveniences of biomass fuels (Saidur et al., 2011a; Stam et al., 2010; Tortosa-Masiá et al., 2005; Wang et al., 2015).

Table 2.3 Biomass fuels benefits and inconveniences.

Benefits	Inconveniences
▪ Inexhaustible and renewable fuel source,	▪ Incomplete renewable energy source as regards the complete life cycle assessment,
▪ Simply low in contents of C, N, S, trace elements, and ash	
▪ Generally high in contents of volatile matter, Mg, H, O, P, and Ca	▪ Moisture and some trace elements are high,
▪ Best reactivity during conversion,	▪ Low in energy density,
▪ Hazardous emissions mitigation (CO_2, CH_4, NO_x, SO_x and trace elements, and waste separated),	▪ Potential competition with feed and food production,
▪ Soil loss and damage possibility of biodiversity; and relatively low-price source,	▪ Potential emission, hazardous components leaching, and odour while heat treatment and disposal,
	▪ Need a proper harvesting, collection, transportation, and storage cost,

▪ Diversification of fuel supply and energy security reaction of new jobs,	▪ Spread a high deal to particulate pollution and global warming during directly burned,
▪ Potential use of oceans and low-quality soils, and restoration of degraded lands; and reduction of biomass-containing wastes,	▪ Biomass resources are quite diffuse and may not be available in sufficient quantities to make a national impact as an energy use.
▪ More costs for electricity generation.	▪ Can cause combustion-related problems because of unfavourable elements in its biomass.

Source: (Saidur et al., 2011a; Stam et al., 2010; Tortosa-Masiá et al., 2005; Wang et al., 2015).

2.5. Slagging and fouling indices

There are two main types of residual deposits in boilers, slagging index (SI) and fouling index (FI). SI refers to furnace deposits, in areas directly exposed to flame radiation such as furnace walls and some widely spaced pendant super-heaters. It takes place in the hottest parts of boiler. While deposits in areas not directly exposed to flame radiation such as the more closely spaced tubes in convection sections of boiler are called FI and it takes place as flue gas and suspended fly ash cool down. Fig. 2.5 shows alkali elements in gaseous form in reaction and the cause of SI on heating surfaces in boilers (Wang et al., 2012) while the other in Fig. 2.6 presents SI and FI in a pulverized fuel boiler (Tortosa-Masiá et al., 2005). Char is combusted to produce the heat required for the process of pyrolysis. After pyrolysis process of a biomass, about 20% of char is obtained. Inorganic elements of char can be sticking on the surfaces of the combustion unit and this is called FI, during char is combusted. Furthermore, it becomes sticky and after cooling, it forms a glassy layer called SI, when these deposits start melting. Burning a fuel containing ash is found to have a negative effect on the efficiency of boilers. The elemental compositions, such as KCl, K_2SO_4, Na_2SO_4, NaCl, and mainly K_2O in ash will lower the ash melting temperature and so enhance the adhesion of fly ash particles. Fly ash particles can cause FI in regions of heat transfer of the boiler. This reduces efficiency of boiler performance and increases maintenance frequency (Al, 2012; Wang et al., 2012). At palm oil factory, SI and FI in combusting EFB boilers effect the routine production, period and cost of cleaning.
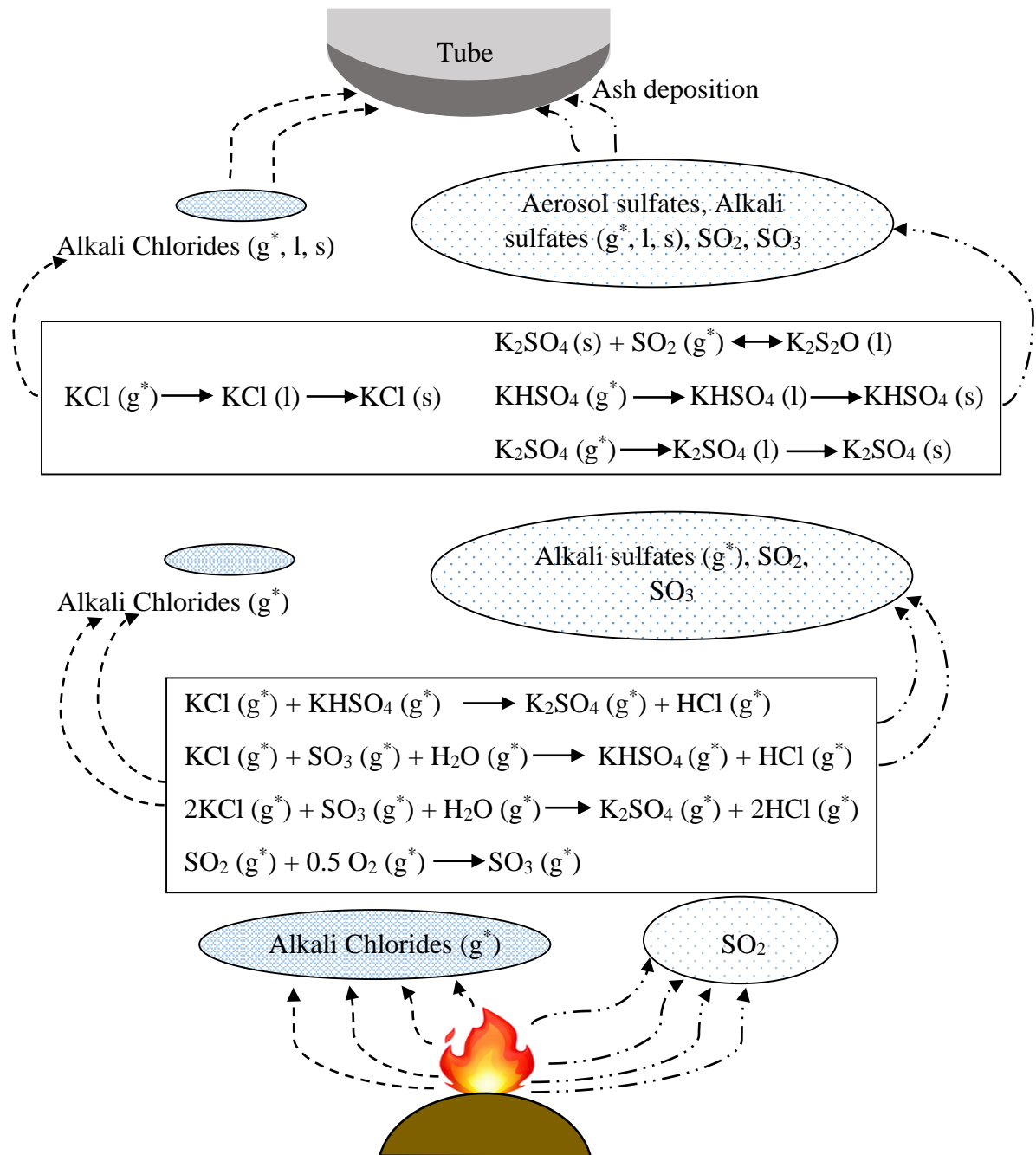
Fig. 2.5 Alkali elements in gaseous form in reaction (gaseous (g^*), liquid (l), solid (s)) and the cause of SI on heating surfaces in boilers (Wang et al., 2012).

Potassium (K), sodium (Na), calcium (Ca), phosphorus (P), and magnesium (Mg) are known as ash produced by either biochemical or thermochemical processes from the chemical breakdown from biomass fuel. The combination of these alkali metals in biomass fuel with other ash contents

becomes major effects on FI and SI in biomass energy conversion system. K and Na are the proxy of ash (Abdullah & Sulaiman, 2013; Novianti et al., 2015).
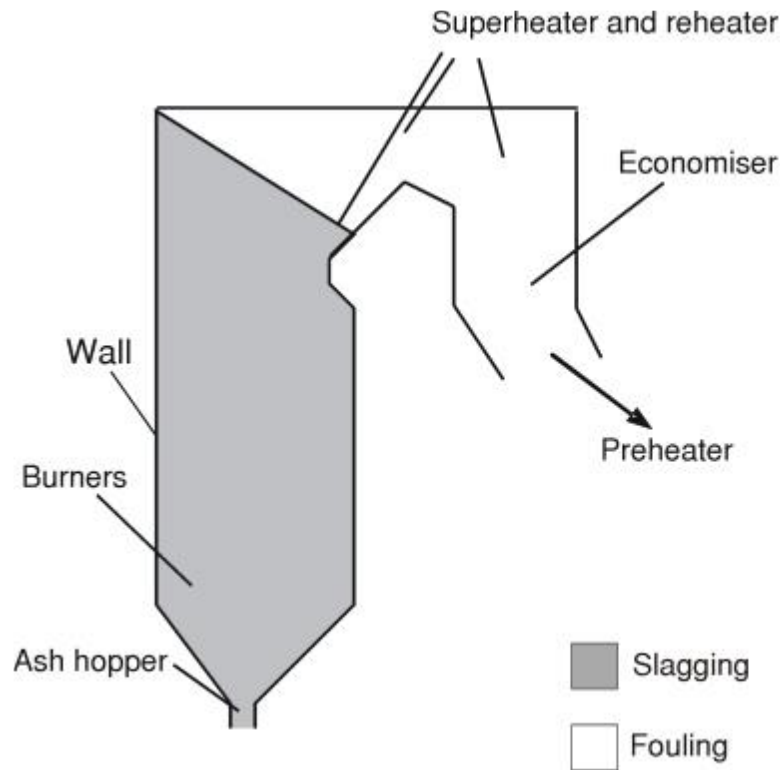
Fig. 2.6 SI and FI in a pulverized fuel boiler (Tortosa-Masiá et al., 2005).

Ash content in biomass actively encourage secondary reaction of thermochemical process, consequence of this producing non-homogenous liquids but EFB with ash content of less than 3 % dry wt is capable for homogenous bio-oil production by fast pyrolysis for petroleum application. In the process of pyrolysis, K is a catalyst and it serves as a dominant source of alkali in most of the biomass fuel. Furthermore, K salts increase char and gas yields. In opposite, they decrease the primary decomposition of liquid products; therefore, K should be low in biomass to receive higher yield in liquid products via fast pyrolysis process (Abdullah & Sulaiman, 2013). Fig. 2.7 shows the boiler SI and FI deposits on boiler tube that use stoker-fired grate furnaces, suspension

units or fluidized beds. Particularly, K in ash ends up in various unfavorable forms (i.e. KCl, K_2SO_4, and K_2CO_3) that have low melting temperatures,; and it can improve the potential formation of deposit (Mettanant et al., 2009; Miles et al., 1995; Rahbari, 2011; Steenari et al., 2009; Turn et al., 1998; Wang et al., 2015). The potential and adverse oxide compounds from ash-forming-oxide during combustion using biomass and the determination of major SI and FI indices can directly be seen and evaluated in Table 2.6 (Nutalapati et al., 2007; Pronobis, 2005; Zhu et al., 2014).
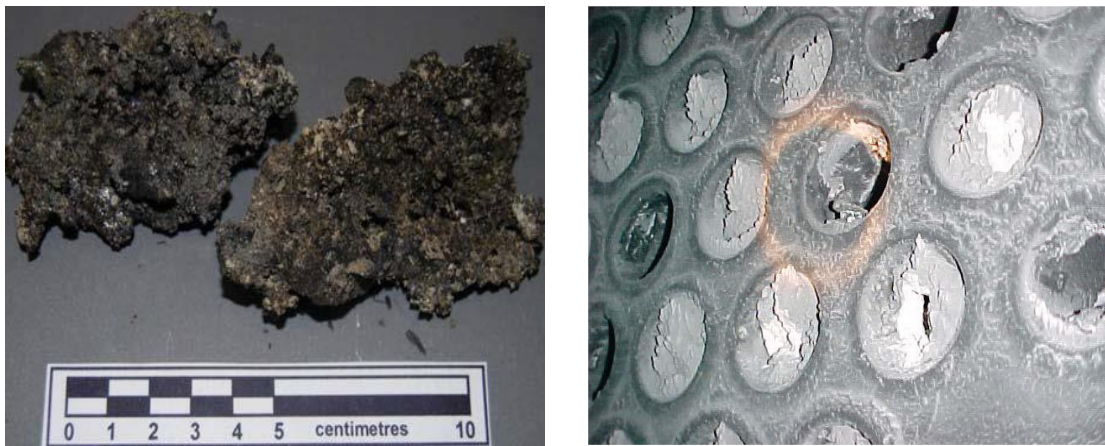
Fig. 2.7 Boiler SI and FI on boiler tubes (Rahbari, 2011; Steenari et al., 2009).

The other number of literature also reported that major inorganic elements such as potassium (K), phosphorus (P) and others are used in general plantation practices presented in Table 2.4 (Abdullah & Sulaiman, 2013; Jinn et al., 2015); they will boost the fruit crops quality and yield, but they create SI and FI deposits when it comes to combustion.

Table 2.4 Major inorganic characteristics of EFB.

Inorganics	Value (mg/kg)	Reference
Potassium (K)	13,028	(Jinn et al., 2015)
	86,100	(Abdullah & Sulaiman, 2013)
Aluminium (Al)	7.30	(Jinn et al., 2015)
	not available	(Abdullah & Sulaiman, 2013)
Calcium (Ca)	804	(Jinn et al., 2015)
	14,300	(Abdullah & Sulaiman, 2013)
Ferrum (Fe)	249	(Jinn et al., 2015)
	2,900	(Abdullah & Sulaiman, 2013)
Magnesium (Mg)	1,148	(Jinn et al., 2015)
	1,900	(Abdullah & Sulaiman, 2013)
Sodium (Na)	124	(Jinn et al., 2015)
	3,300	(Abdullah & Sulaiman, 2013)
Phosphorus (P)	426	(Jinn et al., 2015)
	10,600	(Abdullah & Sulaiman, 2013)
Silicium (Si)	113	(Jinn et al., 2015)
	19,500	(Abdullah & Sulaiman, 2013)

Table 2.5 affirms the major elements in EFB biomass compared to those in various biomasses (Jensen et al., 1998). The industrial and agricultural biomasses namely EFB, millet husk, bagasse, rice straw, rice husk, corn stalks, and coconut shell contain normally the minerals and inorganics such as Al, Ca, Fe, K, and others. EFB tends to have much in amount of substances. However, K in EFB is one of the most contained element and it is the major adverse element for combustion system.

Table 2.5 Main elements in biomasses.

Biomass	Major elements (mg/kg)							
	Al	Ca	Fe	Mg	Na	K	P	Si
EFB	na	14,300	2,900	1,900	3,300	86,100	10,600	19,500
Millet husk	na	6,255	1,020	11,140	1,427	3,860	1,267	150,840
Bagasse	na	1,518	125	6,261	93	2,682	284	17,340
Rice straw	na	4,722	205	6,283	5,106	5,402	752	174,510
Rice husk	na	1,793	533	1,612	132	9,061	337	220,690
Corn stalks	1,911	4,686	518	5,924	6,463	32.0	2,127	13,400
Coconut shell	73.0	1,501	115	389	1,243	1,965	94.0	256

na: Not available.
Source: (Jensen et al., 1998).

Different raw biomass materials contain various inorganic elements not only for types, but also for amount and it also produces the different ash-forming compounds (oxides composition) when it comes to combustion at contrasting furnace designs and temperatures ($\leq$ 815 to 1241 ºC) (Khan et al., 2009; Novianti et al., 2015; Pronobis, 2005; Teixeira et al., 2012). Hence, SI and FI may vary depending on biomasses. Table 2.7 presents the base/acid ratio, SI, and FI tendency in various materials from the literatures. These indices evaluation and limits (i.e. slight, moderate, and high) were determined following by Zhu et al., 2014 (Table 2.6). The limits of these indices damage the combustion or boiler at power plant. So pretreatment methods are the vital techniques needed on biomass materials quality improvement to remove mineral, alkaline or inorganic elements prior to combustion.

Table 2.6 Slagging and fouling indices evaluation.

Indices	Expression, wt %	Limit	
Base/acid ratio (B/A)	$\dfrac{(Fe_2O_3 + CaO + MgO + Na_2O + K_2O)}{(SiO_2 + Al_2O_3 + TiO_2)}$	< 0.21 0.21-0.40 > 0.40	Slight Moderate High
Slagging index (SI)	(B/A)*S^d S^d = % of S in dry fuel	< 0.60 0.60-2.00 2.00-2.60 > 2.60	Slight Moderate High Extremely high
Fouling index (FI)	(B/A)*($Na_2O + K_2O$)	< 0.60 0.60-40.0 > 40.0	Slight High Extremely high

Source: (Nutalapati et al., 2007; Pronobis, 2005; Zhu et al., 2014).

Table 2.7 Slagging and fouling indices tendency in various materials.

Material	B/A ratio (% dry wt)	SI (% dry wt)	FI (% dry wt)
Polish coal[1]	0.40 (moderate)	0.20 (slight)	1.40 (high)
Colombian coal[1]	0.20 (slight)	0.10 (slight)	0.60 (high)
Straw[2]	0.95 (high)	0.11 (slight)	30.9 (high)
Coal[2]	0.56 (high)	0.74 (moderate)	1.98 (high)
Sludge[2]	1.50 (high)	1.70 (moderate)	10.6 (high)
Bone meal[2]	4.03 (high)	4.20 (extremely high)	16.3 (high)
Wheat straw[3]	0.99 (high)	0.20 (slight)	34.2 (high)
Sunflower pellets[3]	18.6 (high)	1.86 (moderate)	429 (extremely high)
EFB[4]	3.17 (high)	0.38 (slight)	1.84 (high)
EFB (this study)	5.40 (high)	0.30 (slight)	334 (extremely high)

Source: (Teixeira et al., 2012)[1], (Pronobis, 2005)[2], (Khan et al., 2009)[3,] and (Novianti et al., 2015)[4].

2.6. Pretreatment methods

2.6.1. Types of pretreatments

Pretreatment is a decisive step for biochemical conversion of lignocellulosic biomass into, i.e. bioethanol (Harmsen et al., 2010). Technologies of pretreatment have their origin in wood science for pulp and paper fabrication but also in crop and agricultural sciences to improve the forage digestibility by ruminants (Rabemanolontsoa & Saka, 2016). According to literature, there are three main category of pretreatment methods, including physical, chemical, and biological pretreatments. Physical pretreatment refers to treatment techniques that are not required the use of either chemicals or microorganisms during the processes. Chemical pretreatment is group of pretreatments which are purely initiated by chemical reactions for disruption of lignocellulosic biomass structure. Biological pretreatment is group of pretreatments that use microorganisms like brown, white, and soft rot-fungi to degrade hemicellulose and lignin. Fig. 2.8 presents pretreatment schematic of goals on lignocellulosics (Mosier et al., 2005). Table 2.8 shows the different kinds of pretreatments from the main pretreatments, substrates, and advantages of pretreatments.
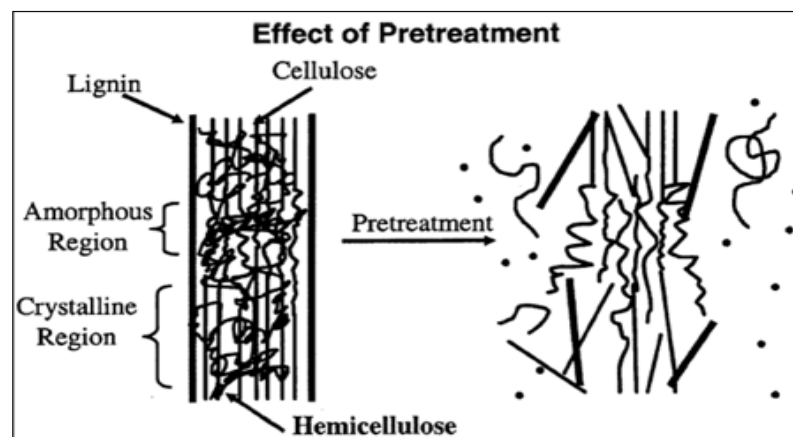
Fig. 2.8 Pretreatment schematic of goals on lignocellulosic biomass (Mosier et al., 2005).

Table 2.8 Variety of pretreatments and individual advantages.

Pretreatment	Substrate	Advantage
Physical pretreatment[1] (steam explosion, comminution, liquid hot water or thermal)	▪ Grass (bulrush, miscanthus, seaweed, hybrid grass), ▪ Softwood (bamboo), ▪ Hardwood (willow, birch, Japanese cedar) ▪ Municipal solid waste (MSW organic fraction, paper tube residues), ▪ Forest residues (mirabilis leaves), ▪ Agricultural residues (EFB, corn stalks, digested bio-fibers, rice straw, clover, bagasse, coconut fiber, banana peel, sunflower).	▪ Heat with high pressure saturated steam on biomass particles for a short period of time. The pressure is swiftly reduced to terminate the reactions that causes biomass to undergo the explosive decompression, ▪ Reduce biomass particle size. Be mostly applied for biofuel processes prior to other pre-treatments in order to improve feedstock handling and treatment, ▪ Hydrate, solubilize, and slightly remove cellulose, hemicellulose, and lignin, respectively. Affect highly for enlarging the accessible and susceptible surface area of cellulose and improve cellulose degradability to microbes and enzymes. Enhance sugar extraction, pentose recovery, and cellulose degradability.

Table 2.8 (Cont.)

Pretreatment	Substrate	Advantage
Chemical pretreatment[2] (acid, alkaline, oxidative)	▪ Grass (grass hay, switch grass, smooth cord grass, wheat grass), ▪ Softwood (spruce, pine), ▪ Hardwood (birch, willow), ▪ Municipal solid waste (newsprint, organic fraction, paper pulp, waste newspaper, yard waste, paper sludge), ▪ Forest residues (fallen leaves), ▪ Agricultural residues (EFB, cakes, sunflower, greenhouse residues, sugarcane bagasse, stalks, coconut fiber, rapeseed, sunflower meals, winter rye straw, bracken, rice straw, corn stover, maize, sugar beet leaves, ensiled hay, wheat straw, digested bio-waste, oilseed rape straw).	▪ Enhance hemicellulose solubilisation and make the cellulose better accessible, ▪ Remove lignin, hemicellulose, and/or cellulose, rendering lignocellulosic biomass more degradable to microbes and enzymes. Be believed to be the saponification and cleavage of lignin carbohydrate linkages. ▪ Remove hemicellulose and lignin to increase the accessibility of the cellulose. Several reactions can take place such as electrophilic substitution, displacement of side chains, cleavage of alkyl aryl ether linkages or the oxidative cleavage of aromatic nuclei.

Table 2.8 (Cont.)

Pretreatment	Substrate	Advantage
Biological pretreatment[3] (fungal, microbial, enzymatic)	▪ Grass (jose tall wheatgrass, napier grass), ▪ Hardwood (Wood chip, Japanese cedar), ▪ Municipal solid waste (pulp/paper sludge), ▪ Agricultural residues (EFB, spent hops, sweet chestnut leaves, sugar beet pulp, cassava residues, manure bio-fibers, corn stalks corn straw, cotton stalks).	▪ Degrade lignin and hemicellulose, while utilize little cellulose. Cellulose is more recalcitrant to fungal attack than other components. Result in increased digestibility of cellulose, which is preferred for anaerobic digestion to enhance biogas production, ▪ Hydrolyze cellulose and hemicellulose into their monosugar counterparts, ▪ Increase biogas production of lignocellulosic biomass, enzymes with hydrolytic activity, which is prior to anaerobic digestion of biomass.

Source: (Zheng et al., 2014; Kratky and Jirout, 2011; Sun and Cheng, 2002; VanWalsum et al., 1996; Hendriks and Zeeman, 2009)[1], (Hendriks and Zeeman, 2009; Zheng et al., 2014; Tarkow and Feist, 1969; Hon and Shiraishi, 2001)[2], and (Zheng et al., 2014; Sun and Cheng, 2002; Rabemanolontsoa and Saka, 2016; Vervaeren et al., 2010)[3].

2.6.2. **Hydrothermal treatment of palm empty fruit bunch**

Hydrothermal treatment is a pressurized thermal conversion process in the water/saturated steam media conducted at a relatively low temperature of 100-230 °C, with or without the usage of citric acid and metal ions catalyst . In other words, hydrothermal treatment techniques/methods is the use of water and temperature together to boil/treat sample or biomass. An improvement in the fuel qualities of EFB like higher energy density, carbon content and lower O/C and H/C ratios compared with the raw feedstock after the hydrothermal treatment process from previous studies on hydrothermal treatment of EFB had been revealed (Nurdiawati et al., 2015a).

The meaning of hydrothermal treatment has undergone several changes from the original Greek meaning of the words 'hydros' means water and 'thermos' means heat. For advanced materials processing, hydrothermal technique is becoming one of the most important tools and hydrothermal treatment can upgrade the raw biomass into more hydrophobic, more stable and more lignin containing feedstock (Byrappa & Adschiri, 2007; Novianti et al., 2016). In other words, for higher density of coal-like fuel for many applications, hydrothermal treatment has been applied for the conversion of raw biomass. For more, hydrothermal treatment is capable of removal of inorganic matters including K, P, Ca, S, Mn, and Mg (Lam et al., 2011; Reza et al., 2013).

Chemical structure which is polymer, known as lignocellulosic, of biomass is dominated by cellulose, hemicelluloses, and lignin components. Cellulose, functions as a frame in the form of microfibrils. Hemicellulose covers these long-chained cellulose microfibrils in matrix form. The microfibrils are linked by a huge bond with lignin, as structural filler, forming the fibrils. Besides, biomass contains extractives, non-forming structural compounds that easily dissolved in water or organic solvents, and ash (Prawisudha et al., 2014).

Hydrothermal treatment process is one of the methods to improve biomass quality through carbonization. Biomass will receive conductive heat from water media during this process. There will be the decomposition of carboxyl, hydroxyl ether and ester in biomass and resulting in higher C/O and C/H ratio in solid (Lam, 2013).

Typically, hydrothermal processes will result in the hydrolysis of the more accessible hemicellulose fraction, and soluble sugar monomer or oligomer formations. To improve the enzyme digestibility of lignocellulosic feedstock, hydrothermal treatment is needed. It is presumed to increase the porosity of the remaining cellulose rich residue by allowing greater access by cellulose enzymes, especially in the critical nanometer regime. As a proof, a number of studies had shown that the lignin phase is disrupted under hydrothermal conditions as well, which must also impact on cellulose accessibility (Ibbett et al., 2011).

Products from hydrothermal treatment will be physically degraded and will result in smaller size and more uniform products. One hindering problem is its high inorganic constituents particularly its potassium content, in case of enhancing the palm oil EFB quality. The reaction/combination between K and O will produce compound in the form of slag (Prawisudha et al., 2014). It is reported that the slag forming inside furnace can shorten the duration of furnace maintenance and increases the cost of maintenance in order to maintain the furnace (ISTA, 1999). Since the EFB structural cell will be broken by high temperature and K^+ ion will be easily removed and reacts with water, hydrothermal treatment process is expected to support the reaction (Prawisudha et al., 2014). Potassium ion (K^+ ion) will likely react with OH^- ion in the water; thus it is mentioned that one another method to reduce/remove the content of K is water washing (Sun et al., 2013). The chemical reactions (Eq. 1 and Eq. 2) will be shown below.

$$4K^+ \text{ (s)} + O_2 \text{ (g)} \rightarrow 2K_2O \text{ (s)} \qquad (1)$$

$$K^+ \text{ (s)} + H_2O \text{ (l)} \rightarrow KOH \text{ (l)} + 2H^+ \qquad (2)$$
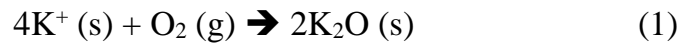
Table 2.9 shows the different hydrothermal treatment and percentage of K removal from reviews. Hydrothermal treatment at 180 ºC seems more preferred for the large-scale production of solid fuel from EFB, by considering the energy yield of the ash content of the product and the energy requirement. Nutrient solubilisation linearly increased as the reaction temperature was increased (Nurdiawati et al., 2015b). In some studies above on hydrothermal treatment of EFB had shown that most temperatures used are higher than 100 ºC. However, using of the temperature at lower or equal to 100 ºC mean to save energy and they are also practical temperatures (Kumar et al., 2009).

Table 2.9 Effects of ambient and thermal treatment methods on potassium removal of various biomasses.

Material	Size	Method	Reaction temperature	Detention time	Potassium removal
EFB	1-2 cm	Hydrothermal using autoclave reactor[1]	150, 175 and 200 ºC	30min	- Up to 77 % at 150 ºC - Up to 64 % at 200 ºC
	1 cm	Hydrothermal using autoclave reactor[2]	100, 150, 180 and 220 ºC	30min	- 54.9 % at 100 ºC - 74.1 % at 180 ºC
	1 cm	Combined hydrothermal and water washing[2]	Hydrothermal: 100, 150, 180 and 220 ºC Water washing: 60 ºC	- Hydrothermal: 30min - Water washing: 15min	- 82 % at 100 ºC - 92 % at 180 ºC
	1-3 cm	Water washing[3]	25-28 ºC (ambient temperature)	5-30min	- 71 % at 25-28 ºC, 30min - 39 % at 25-28 ºC, 5min
Corn stover	1.8 cm	Hydrothermal carbonization[4]	200, 230 and 260 ºC	5min	- 27.5 % at 200ºC - 59.9 % at 230ºC
Miscanthus	1.8 cm	Hydrothermal carbonization[4]	200, 230 and 260 ºC	5min	- 12.26 % at 200ºC - 59.4 % at 230ºC
Switch grass	1.8 cm	Hydrothermal carbonization[4]	200, 230 and 260 ºC	5min	- 2.85 % at 200ºC - 72.65 % at 260ºC
Rice hulls	1.8 cm	Hydrothermal carbonization[4]	200, 230 and 260 ºC	5min	- 80.43 % at 230 ºC - 86.96 % at 260 ºC
Sugarcane bagasse	≤ 0.025 cm	Water leaching[5]	25 ± 2 ºC	Soaking/leaching time: 1 h	92 %

nd: Non-defined.

Source : (Prawisudha et al., 2014)[1], (Novianti et al., 2015)[2], (Abdullah & Sulaiman, 2013)[3], (Reza et al., 2013)[4], and (Das et al., 2004)[5].

CHAPTER 3

MATERIALS AND METHODS

3.1. Substrate collection and preparation

Fresh EFB of species Elaeis guineensis before pressing process was firstly collected from Chumporn Palm Oil Industry in Thasae District, Chumporn Province, Thailand (N10º50´30.0´´, E99º13´16.2´´) and then it was immediately sun dried in order to get rid out of fungus growth causing by high moisture and to reduce in size. This fresh EFB was suddenly analysed for total solids (TS), volatile solids (VS), and ash content as the basic raw characteristics. Fresh EFB was sun dried for 7 days to get the proper dry EFB based on its lowest moisture content remaining. After had dried, it was then shredded into 2-5 cm followed by sieving to remove undesired elements prior to the experiments. Also, a portion of fresh EFB was oven dried at 60 ºC prior to determine its other raw characteristics as shown in Table 3.1 and Table 3.2; and analytical methods present in section 3.4.

Table 3.1 Characteristics of raw EFB used in this study.

Parameter	Value	Unit
Proximate analysis		
Total solids, TS	419	g/kg wet
Moisture content, MC	581	g/kg wet
Volatile solids, VS	949	g/kg dry
550 ºC ash	5.20	% dry wt
850 ºC ash	4.60	% dry wt
Fiber composition		
Cellulose	47.7	% dry wt
Hemicellulose	20.2	% dry wt
Lignin	10.5	% dry wt
Other characteristics		
Total oil	49.1	g/kg
Higher heating value, HHV	18.6	MJ/kg
Slagging index, SI	0.30	% dry wt
Fouling index, FI	334	% dry wt

Table 3.2 Inorganic element and oxide compounds of raw EFB.

Parameter	Formula	Value	Unit
Inorganic element			
Barium	Ba	77.9	mg/kg
Aluminium	Al	99.2	mg/kg
Silicon	Si	161	mg/kg
Sodium	Na	394	mg/kg
Phosphorus	P	745	mg/kg
Magnesium	Mg	1,402	mg/kg
Calcium	Ca	2,149	mg/kg
Potassium	K	20,467	mg/kg
Oxide compounds (ash analysis)			
Aluminium oxide	Al_2O_3	0.20	% dry wt
Rubidium oxide	Rb_2O	0.30	% dry wt
Sulfur trioxide	SO_3	1.80	% dry wt
Iron (III) oxide	Fe_2O_3	1.90	% dry wt
Magnesium oxide	MgO	2.60	% dry wt
Phosphorus pentoxide	P_2O_5	2.70	% dry wt
Calcium oxide	CaO	6.80	% dry wt
Silicon dioxide	SiO_2	13.4	% dry wt
Potassium oxide	K_2O	61.8	% dry wt
Chloride	Cl	8.60	% dry wt

3.2. Experimental design

In this work, ambient temperature and hydrothermal treatments batches were performed in order to either compare or evaluate the effects of treatments on K removal from EFB as well as SI and FI reduction. However, hydrothermal treatment batch was the main and focused one. There are 3 independent variables for the both batches of treatment (ambient temperature and hydrothermal treatments), including total solids (TS) of 50, 75, and 100 g/L, temperature of 28-30 (ambient temperature), 60, and 120 ℃, and detention time of 0 (control), 30, 60, and 120 min. In order to get each TS concentration (g/L), the dry EFB sample was firstly divided by weight into various TS of 50, 75, and 100 g and were loaded into 2 L stainless steel containers in accordance with

different treatments needed. Then each 1L distilled water was poured on each TS weight loaded to get TS of 50, 75, and 100 g/L prior to the treatments, respectively.

The ambient temperature treatment was carried out in ambient air at temperature of 28-30 °C. It was separated in 2 sets, the first one is known as washing or control set which was done for the first flushing or pouring of distilled water on EFB sample considered as detention time of 0 min and another one is known as soaking set which was run for detention time of 30, 60, and 120 min. In addition, major hydrothermal treatment experimental performance was treated at low and practical temperature of 60 and 120 °C for detention time of 30, 60, and 120 min. Each treatment was done in 3 replicates. At each completed treatment, sample was filtrated with muslin cloth to separate treated EFB and liquid fraction. Continuously, treated EFB was spun with a spin dryer (White Knight 28009W Gravity Drain Spin Dryer, German) at 2800 rpm for 5 min in order to release more liquid fraction prior to drying at 103 °C and for further analyses. Treated EFB sample was determined for particular K content, SEM image before quantitative K content by EDX, oxide compounds in its EFB ash, total oil, and mass balance. The analytical methods are presented in the following section.

3.3. Hydrothermal treatment by lab-scale autoclave

Lab-scale autoclave facility (TOMY Autoclave SS-325, Japan) with the automatic pressure gauge was employed in hydrothermal treatment batch. The operation for this autoclave machine commonly started at 28-30 °C (ambient air) and there was a ramp-up time (Ru) of 25 min and 45 min, which was not counted as working time or detention time, to reach the setting temperature at 60 and 120 °C. At each completed batch of treatment, the exhaust valve was switched to "open" mode to release the residual air and pressure, and to cool the machine down at the same time. At this point, the hot vapor and condensed water

were flowing through the draining port to the cooling box and then the impinger. For more, the ramp-down time (Rd) of 20 min and 40 min was spent to reach down 0 pressure drop for 60 and 120 °C batches, respectively. Finally, the chamber lid cover was ready to open to collect the treated sample for further process. Fig. 3.1 shows the example of ramp-up time (Ru) from ambient air (30 °C) to reach autoclave operation temperatures (60 and 120 °C) for working time of 30 min detention time, and ramp-down time (Rd) for finishing the treating process.
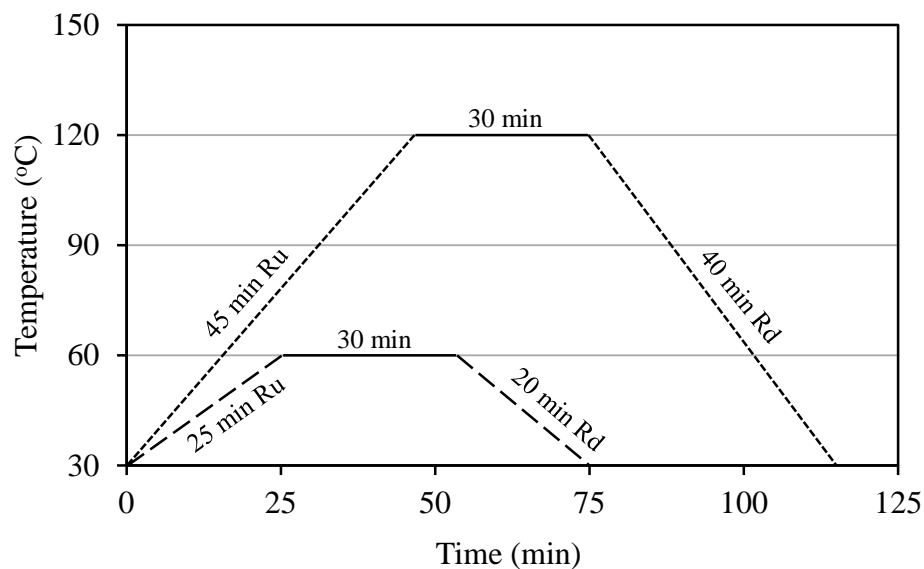
Fig. 3.1 Example of autoclave operation for hydrothermal treatment batch at 60 and 120 °C temperature for 30 min detention time.

3.4. Sample and data analysis

In this section, each parameter and analytical method were respectively described. Total solids (TS), volatile solids (VS), and ash in raw and treated EFB were determined using the modified laboratory analytical procedure for biomass (LAP001 and LAP005) developed by the national renewable energy laboratory (NERL, 1994a; NERL, 1994b). Potassium (K) and other inorganics in raw EFB and K in treated EFB were detected by the inductively coupled plasma optical

emission spectrometry method (ICP-OES, Optima 8000, Perkin Elmer, USA) at different wavelengths (Table 3.3). The K concentration (mg/kg) in raw and treated EFB were compared and K removal (%) was then calculated (Eq. 3). And remaining K (%) can be calculated by following equation (Eq. 4).

$$\text{K removal (\%)} = \frac{\text{(Initial K content) - (Remaining K content)}}{\text{(Initial K content)}} \times 100\% \tag{3}$$

$$\text{Remaining K (\%)} = 100\ \% - \text{K removal (\%)} \tag{4}$$

Table 3.3 Different wavelengths for the analysis of inorganic substances.

Substance	Formula	Wavelength	Unit
Silicon	Si	251.611	nm
Aluminium	Al	396.453	nm
Barium	Ba	233.527	nm
Sodium	Na	589.592	nm
Potassium	K	766.490	nm
Phosphorus	P	213.617	nm
Beryllium	Be	313.107	nm
Calcium	Ca	317.933	nm
Magnesium	Mg	285.213	nm

Raw and treated EFB samples were done analyzing the properties of its fuels in ash generated from tube furnace at 850 °C for 15 min (the temperature and time equivalent to combusting EFB biomass in boiler using at Chumporn oil palm factory). Those properties are major oxide compounds as % dry wt (Fe_2O_3, CaO, MgO, Na_2O, K_2O, SiO_2, Al_2O_3, and TiO_2), which were tested by the X-ray XRF technique. Samples for SI and FI determination were chosen by RSM design; and each 5 treatments (3 replicates) from each TS of 50, 75, and 100 g/L was selected. SI and FI were then determined following Eqs. (5) and (6) (Zhu et al., 2014).

Slagging index $\qquad$ SI (% dry wt) = (B/A) × S^d $\qquad$ (5)

Fouling index $\qquad$ FI (% dry wt) = (B/A) × (Na$_2$O + K$_2$O) $\qquad$ (6)

where $\qquad$ B/A = base/acid ratio = $\dfrac{(Fe_2O_3 + CaO + MgO + Na_2O + K_2O)}{(SiO_2 + Al_2O_3 + TiO_2)}$

$\qquad$ S^d = % dry wt of sulfur in dry EFB fuel

Raw EFB and treated EFB based on its highest K removal were selected and scanned for its cross section view using the scanning electron microscopy (SEM) model Quanta 400, FEI, Czech Republic with an Everhart Thornley detector at voltage 15 kV before EDX analysis. The cross section view from these two samples were then tested for the quantitative K concentration (% dry wt) from the surface to core fiber by EDX (Fig. 4.4). The gross calorific value as HHV in raw EFB was tested by combusting in an adiabatic oxygen-bomb calorimeter following the in-house method based on ASTM D5865 (ASTM, 2013) while total oil of raw and treated EFB was hydrolyzed by acid hydrolysis method and extracted using Soxhlet following the in-house method based on AOAC Official Method 922.06 (AOAC, 2006). Total oil (g/kg) in raw EFB and treat EFB were compared. Potential total oil recovery (%) was then calculated (Eq. (7)).

Potential total oil recovery (%) = $\dfrac{(Initial\ total\ oil) - (Remaining\ total\ oil)}{(Initial\ total\ oil)} \times 100\%$ $\quad$ (7)

3.5. Statistical and multiple regression analysis

Mean and the standard deviation were calculated and used to compare the effects of our independent variables using Excel version 2013. The experimental design for K removal was conducted using full factorial design. The first independent variable X_1 is total solids (g/L) was tested at 3 levels (50, 75, and 100 g/L), and the second independent variable X_2 is temperature (°C) was studied at 3 levels (30, 60, and 120 °C), while the third independent variable X_3 is detention time (min) at 3 levels (30, 60, and 120 min). A total of 27 treatments were run in triplicate (81 data sets) with K removal (Y) as the interested response of the model. A second order polynomial equation (Eq. (8)) was employed to fit the experimental data using the Design Expert Trial Version 7.0.0. Coefficients with statistical significance were indicated at $p < 0.05$. Response two-dimension contour plots were generated with the mentioned software.

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_1^2 + b_5X_2^2 + b_6X_3^2 + b_7X_1X_2 + b_8X_1X_3 + b_9X_2X_3$$

(8)

where Y is the predicted response , b_0 is a constant, b_{1-3} are the linear coefficients, b_{4-6} are the squared coefficients, b_{7-9} are the cross-product coefficients, and X_{1-9} are the actual values of the studied independent variables. The response of K removal was regressed with respect to total solids (g/L), temperature (°C), and detention time (min).

3.6. Determination of mass balance

Mass balance is the combination between mass loss in term of solid particle loss or TS loss, remaining TS, remaining MC and MC loss as kg through the process flows. First, the 1 ton EFB_{wet} was sun drying. Then the remaining TS was cutting and sieving following by treating with hydrothermal treatment, spinning, and finally drying (103 $^{\circ}$C) processes. After sun drying process, the remaining TS was calculated via the known value of total moisture loss. This amount of remaining TS was continuously passed by cutting and sieving, then the remaining TS after these processes was calculated through the known value of solid particle loss. For hydrothermal treatment process to drying (103 $^{\circ}$C) process, the best treatment of 50 g/L (at 120 $^{\circ}$C for 120 min) was chosen as a basic TS for mass balance as well as other major parameters determination. Fig. 3.2 shows each process flow which began with 1 ton of fresh EFB (EFB_{wet}) until drying process at 103 $^{\circ}$C, then other important parameters including TS, VS, ash, K, total oil, SI, and FI will be calculated and fuel quality of EFB will be discussed. The completed diagram of mass balance by each process shows in Fig. 4.5 in section 4.6.
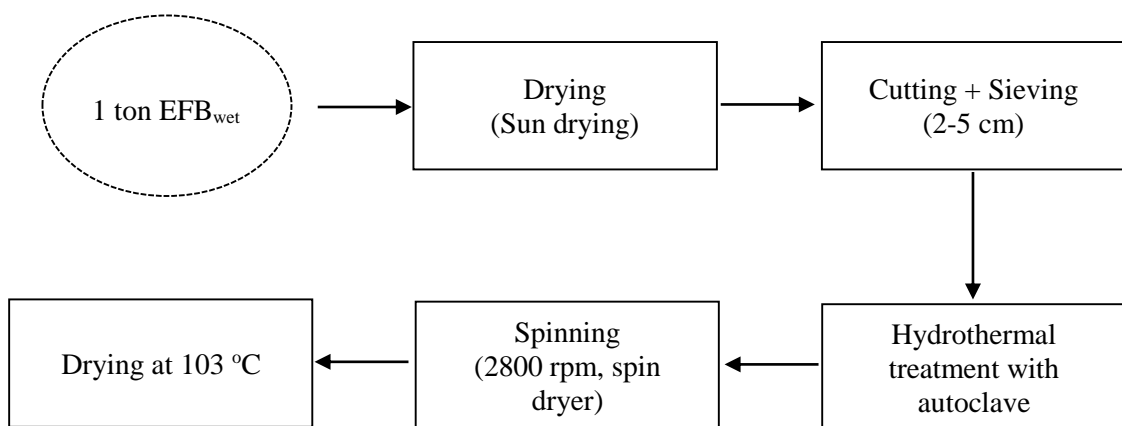
Fig. 3.2 Process flow for mass balance evaluation.

3.7. Overall experimental diagram

The closure for materials and methods part is the section of overall experimental diagram. It concludes the starting from substrate collection and preparation, experimental design, autoclave operation, sample and data analysis, statistical and multiple regression analysis, and determination of mass balance, respectively (Fig. 3. 3).
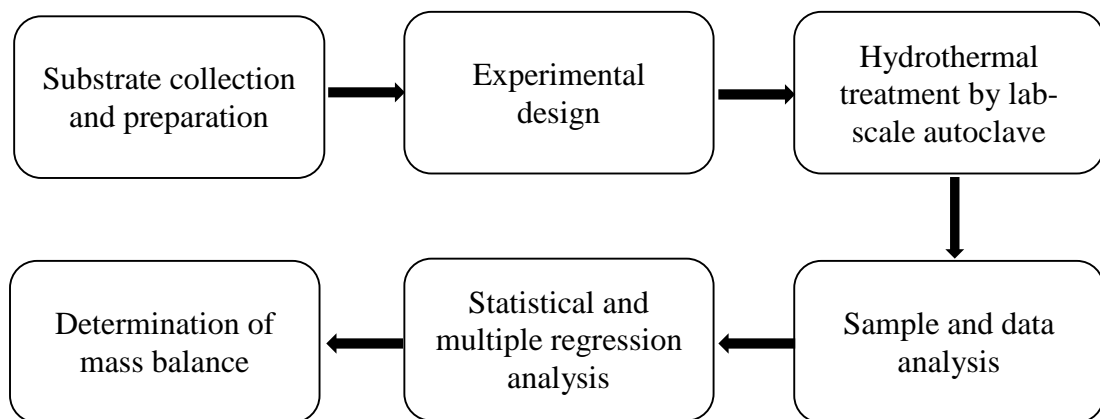
Fig. 3.3 Overall experimental diagram.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Remaining potassium concentration

In this work, potassium (K) concentration was not only found remaining in treated EFB sample after hydrothermal treatment but also after ambient temperature treatment and the first washing on EFB (considered as detention time of 0 min). It might be the treatment temperature is not high enough for hydrothermal treatment method. Fig. 4.1 presents the data of remaining K concentration in mg/kg from treatments under three various total solids concentrations of EFB (50, 75, and 100 g/L) at three temperatures (30, 60, and 120 ^{o}C) for three detention times (30, 60, and 120 min). Results showed that medium remaining K concentration in treated EFB sample under ambient temperature treatment at low temperature of 28-30 ^{o}C for detention time of 30 min are only 3,584 ± 22.1, 3,804 ± 54.3, and 5,523 ± 471 mg/kg for 50, 75, and 100 g/L, respectively. In opposite, the lowest K remaining in EFB was found in hydrothermal treatment batch at highest temperature of 120 ^{o}C for longest detention time of 120 min with the amount of 1,910 ± 14.4, 2,301 ± 210, and 2,468 ± 173 mg/kg for three different total solids, respectively. The low remaining is because of this K inorganic substance was already released out from EFB at the first flushing or washing by distilled water considered as detention time of 0 min at temperature of 28-30 ^{o}C and remained with only the value of 9,887 ± 643 mg/kg in EFB. Previous literatures cited that OH$^-$ ion is a factor found to be influencing K removal, potassium ion (K$^+$) will likely react with OH$^-$ ion in the water; so that it can be highly solubilized by water (Knudsen et al., 2004; Prawisudha et al., 2014; Sun et al., 2013). Therefore, a demonstration that simple biomass washing by distilled water in the room atmosphere (28-30 ^{o}C) could remove simple alkali substances which dissolve easily. Previous researchers confirmed that 60 to 90 % of the K and others like Na, Cl, and S may

capably remove from biomass by washing (Deng et al., 2010). In this experiment, low total solids of 50 g/L provided less K remaining than higher total solids of 75 and 100 g/L at all temperature (30, 60, and 120 ºC) in reason that lower total solids concentration in the bulk liquid promotes higher concentration gradient between K in EFB fiber and that in bulk liquid. K remaining does not show significant different at highest temperature of 120 ºC for shortest detention time of 30 min to longest detention time of 120 min under total solids of 50 and 75 g/L. This might be K in EFB fiber could already leached out from EFB and remained less in amount in EFB at only $1,952 \pm 91.9$ and $2,354 \pm 150$ mg/kg in the first shortest detention time of 30 min. High total solids loading concentration (100 g/L) gave larger trending of K remaining at different Temp (Fig. 4.1 for 100 g/L). Hence, low total solids loading and long detention time at high temperature can help more K release. It was reported that hydrothermal treatment technique is expected to support the reaction since it loosens the structure of EFB fiber and K ion would easily release and dissolved into water (Prawisudha et al., 2014). In other words, monotonous rate of removal of K can increase when water is in hot phase by increasing temperature (Deng et al., 2010; Zhu et al., 2014).

Best treatment condition of 50 g/L at 120 ºC for 120 min, which is one of RSM selected condition, under this lab-scale hydrothermal treatment is recommended for the industry since it could remove K up to 90.7 ± 0.10 % (or $1,910 \pm 14.4$ mg/kg remaining). Moreover, SI and FI are acceptable for this treatment compared to other treatments which they were reduced to the lowest at 0.07 ± 0.00 % dry wt and 38.5 ± 0.60 % dry wt. These both indices still indicate the presence of their limits occurring in EFB ash with slight and high phases compared to those of the standard limits (Zhu et al., 2014).
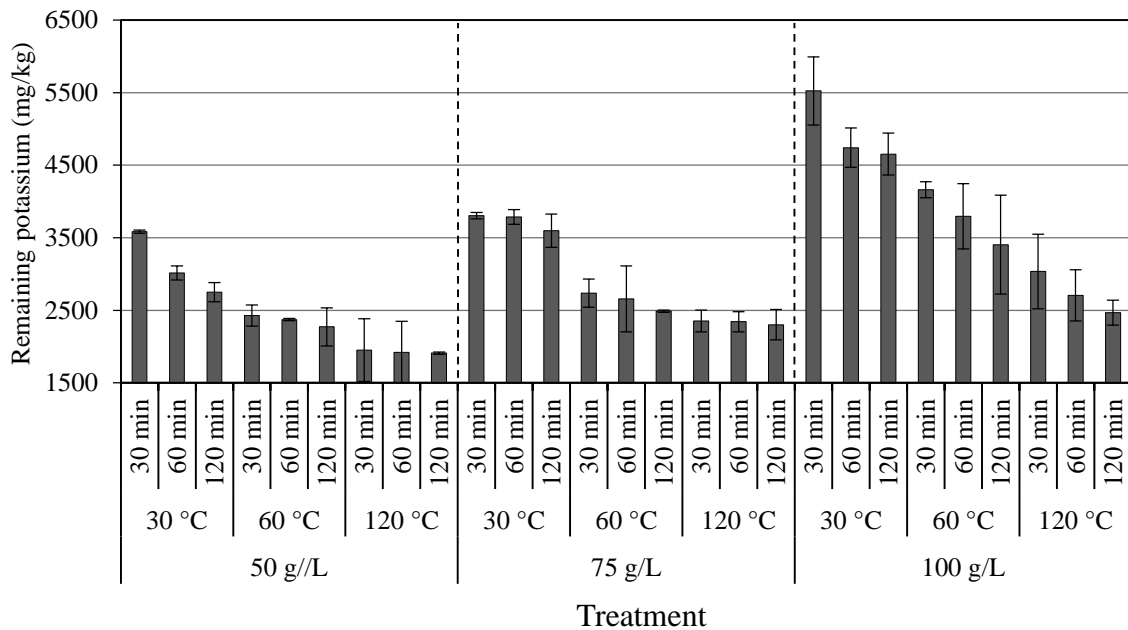
Fig. 4.1 Remaining potassium (mg/kg) from treatments under three TS concentration of EFB (50, 75, and 100 g/L) treated at temperature of 30, 60, and 120 °C for detention time of 30, 60, and 120 min.

4.2. Relation of remaining K versus SI and FI

To confirm the effectiveness of treatments on slagging index (SI) and fouling index (FI), remaining K (%) was plotted against them in order to see how they are correlated. There are 2 main reasons why K was the only inorganic selected for the relation, including K itself is the most restrained substance in EFB fiber and the literatures also reported that this inorganic K is the most adverse element causing SI and FI when it comes to combustion (Abdullah & Sulaiman, 2013; Baharuddin et al., 2009; Geng, 2013). The linear function was chosen to use in order to translate the relation between remaining K to SI and remaining K to FI based on their equations model (Eq. 5 and Eq. 6). However, linear function somehow might not be good for the relation between remaining K versus SI and remaining K versus FI under 50 g/L at lowest values of relation (Fig. 4.2a and Fig. 4.2b) because it was also related to Si element as well as SiO_2, which was increased in amount after treatment and hence it reduced SI and FI (based on Eq. 5 and Eq. 6). Fig. 4.2a and 4.2b show remaining K versus SI and

remaining K versus FI with coefficients R^2 of 0.76-0.98 (Eqs. 9-11) and 0.84-0.97 (Eqs. 12-14), respectively. These high coefficients satisfactorily represent the best inverse correlation between the remaining K to the both indices. The limits of SI and FI in biomass ash as well as in EFB ash increase upon the high presence in value of the unfavorable sulfur (S) and oxides such as iron (III) oxide (Fe_2O_3), calcium oxide (CaO), magnesium oxide (MgO), sodium oxide (Na_2O) and potentially potassium oxide (K_2O) based on their evaluation following Eqs. (5) and (6) in the section 3.4. Thus, removal of these individual components from EFB fiber will reduce SI and FI. Nevertheless, these individual substances were remained negligible compared to K substance for this study, which remained noticeable. Potential K is one of the most serious inorganics causing SI and FI in combustion boilers (Abdullah & Sulaiman, 2013); hence more removing of K from EFB, more reducing of these indices. The limited standards for SI in biomass ash are < 0.60 % dry wt (slight SI occurrence), 0.60-2.00 % dry wt (moderate SI occurrence), 2.00-2.60 % dry wt (high SI occurrence) and > 2.60 % dry wt (extremely high SI occurrence) while for FI in biomass ash are < 0.60 % dry wt (slight FI occurrence), 0.60-40.0 % dry wt (high FI occurrence) and > 40.0 % dry wt (extremely high FI occurrence), respectively (Zhu et al., 2014).

Potassium was resulted in lowest and highest removals at 73.0 ± 3.60 % and 82.5 ± 1.90 % (Fig. 4.2) under two treatments of 50 and 100 g/L at 30 ℃ for 30 min. The total solids of 75 g/L is always in the middle between total solids of 50 and 100 g/L on lowest and highest of potassium removal, SI, and FI. Upon the lowest K removal under the two mentioned treatments, SI and FI were oppositely amounted highest at 0.12 ± 0.00 % dry wt (Fig. 4.2a) and 86.3 ± 0.20 % dry wt (Fig. 4.2b), respectively. On the other hand, they were reduced into lowest value upon the highest K removal. Experimental data approved that K removal was highly leached out from treated EFB at 120 ℃ temperature for 120 min detention time with the value of 90.7 ± 0.10 % under 50 g/L of total solids. Additionally, SI and FI were reduced to the lowest at 0.07 ± 0.00 % dry wt (Fig.

4.2a) and 38.5 ± 0.60 % dry wt (Fig. 4.2b). These both indices still indicate the presence of their limits occurring in EFB ash with slight and high phases compared to those of the standard limits (Zhu et al., 2014), respectively. However, SI and FI were significantly reduced with amount of 0.23 % dry wt (or ~ 76.7 % reduction) and 295 % dry wt (or ~ 88.5 % reduction) compared to raw SI and FI in Table 3.1. Therefore, hydrothermal treatment is positive and sufficient for better EFB fuel production through potassium removal and SI and FI reduction. The result from this study is comparable with the literature on hydrothermal treatment at 180 °C of EFB, which SI was reported 0.33 % dry wt reduced (or ~ 86.8 % reduction); but FI was reported only 1.26 % dry wt reduced (or ~ 68.5 % reduction) compared to their raw SI and FI from the literature (Novianti et al., 2015). The differences are still based on treating condition, material preparation, and characteristics of raw material.
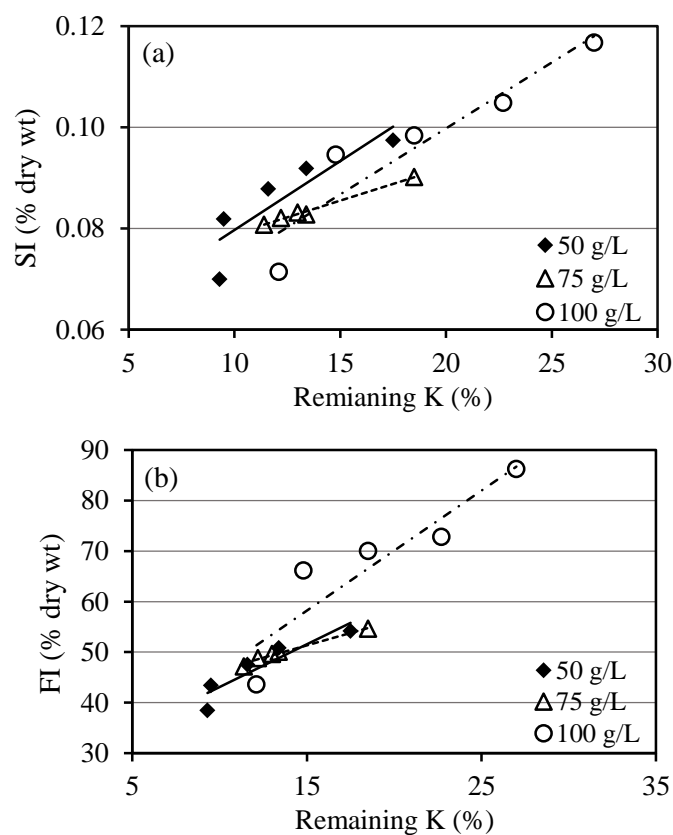

Fig. 4.2 Relation of (a) remaining K vs. SI and (b) remaining K vs. FI of RSM selected treatments.

50 gTS/L : SI = 0.003 Remaining K + 0.05, $\qquad$ R² = 0.76 $\qquad$ (9)

75 gTS/L : SI = 0.001 Remaining K + 0.06, $\qquad$ R² = 0.98 $\qquad$ (10)

100 gTS/L : SI = 0.002 Remaining K + 0.04, $\qquad$ R² = 0.87 $\qquad$ (11)

50 gTS/L : FI = 1.68 Remaining K + 26.2, $\qquad$ R² = 0.85 $\qquad$ (12)

75 gTS/L : FI = 0.98 Remaining K + 36.5, $\qquad$ R² = 0.97 $\qquad$ (13)

100 gTS/L : FI = 2.36 Remaining K + 22.7, $\qquad$ R² = 0.84 $\qquad$ (14)

4.3. Effects of total solids, temperature, and detention time on K removal

Full factorial design was applied in order to find the relationship of total solids (g/L), temperature (ºC), and detention time (min) to K removal (%) with 81 data runs. The good fits of regression model Eq. (15) for K removal was checked by F-test, and Table 4.1 presents the variance (ANOVA) analysis for the quadratic model. The F-test model provided the value of less than 0.0001 for this dependent parameter, indicating that the model was statistically significant ($p < 0.05$). The good fit to experimental data was confirmed by high coefficient R^2 of 0.89, possessing a good predictability. Additionally, the low values of coefficient of variance (CV) satisfied sufficiently precision and reliability for the all treatments performed. All terms in the models were used to generate the two-dimensional contours plots in Fig. 4.3.

K removal (%) = 74.3823 + 0.1025 * total solids + 0.2377 * temperature + 0.0695 * detention time + 0.0011 * total solids * temperature + 0.0005 * total solids * detention time − 0.0003 * temperature * detention time − 0.0024 * total solids^2 − 0.0014 * temperature^2 − 0.0004 * detention time^2

$\qquad$ (15)

Table 4.1 Estimated regression coefficients and ANOVA of fitting model for K removal.

Source	Potassium (K) removal (%)	
	Coefficient estimate	Probability
b_0	74.3823	< 0.0001
$b_1 \times$ total solids	0.1025	< 0.0001
$b_2 \times$ temperature	0.2377	< 0.0001
$b_3 \times$ detention time	0.0695	< 0.0001
$b_4 \times$ total solids $\times$ temperature	0.0011	< 0.0001
$b_5 \times$ total solids $\times$ detention time	0.0005	0.0457
$b_6 \times$ temperature $\times$ detention time	$- 0.0003$	0.0479
$b_7 \times$ total solids^2	$- 0.0024$	0.0005
$b_8 \times$ temperature^2	$- 0.0014$	< 0.0001
$b_9 \times$ detention time^2	$- 0.0004$	0.0801
F-significant	< 0.0001	
R^2	0.8938	
R^2 adjusted	0.8804	
Coefficient of Variance	2.00	

Removing of K from EFB defines the reduction of slagging and fouling from EFB ash. Thus, K removal (%) must be minimized in order to confirm the clean EFB since they affect both the combustion power plant and maintenance. The interactive effects of detention time, temperature, total solids on K removal (Fig. 4.3a-c) were displayed pair-wise whereas third variable was fixed; detention time = 80 min, temperature = 75 °C, and total solids = 75 g/L. According to the contours plots, increasing temperature (°C) while decreasing total solids (g/L) (Fig. 4.3a), increasing detention time (min) while decreasing total solids (g/L) (Fig. 4.3b) and increasing both detention time (min) and temperature (°C) (Fig. 4.3c) resulted in low K removal, respectively. Furthermore, the regression model proved that there is relation of total solids and temperature, total solids and detention time, and temperature and detention time on K removal with high statistical significance of ($p < 0.0001$), ($p < 0.0457$), and ($p < 0.0479$), respectively. These revealed the impacts of all 3 independent variables on K removal; nevertheless, the relation of temperature and total solids seems the most effective ones. The impact of detention time was clearly

noticeable at low total solids (Fig. 4.3b) and high temperature (Fig. 4.3c), even though quadratic detention time^2 term was not highly significant. The optimum K removal is 91 % at each highest temperature and Time under lowest total solids verified by Fig. 4.3 which is coincided with the lowest K remaining of only 1,910 ± 14.4 (~9 % remaining) in Fig. 4.1 at 120 ºC temperature for 120 min detention time under 50 g/L total solids. This is in agreement with Novianti et al., 2015 and Reza et al., 2013, who reported that higher K removal finds at higher temperature.

Potassium (K) is one of the most contained alkalines or inorganics in EFB biomass due to its large quantity required as nutrient. It contributes to the low melting ash of EFB fuel. Thus, thermal treatment application is potential on this constituent removal to increase ash fusion temperature of EFB biomass fiber (Hafiz et al., 2016). Once EFB is in high quality fuel, SI and FI (ash deposits) will be reducing from the combustion system. This is economical for oil palm power plant in term of EFB wastes management and maintenance (ISTA, 1999; Theis et al., 2006; Yaakob et al., 2012).

(a) Total solids vs. Temperature at 80 min

(b) Total solids vs. Detention time at 75 °C

(c) Temperature vs. Detention time at 75 g/L
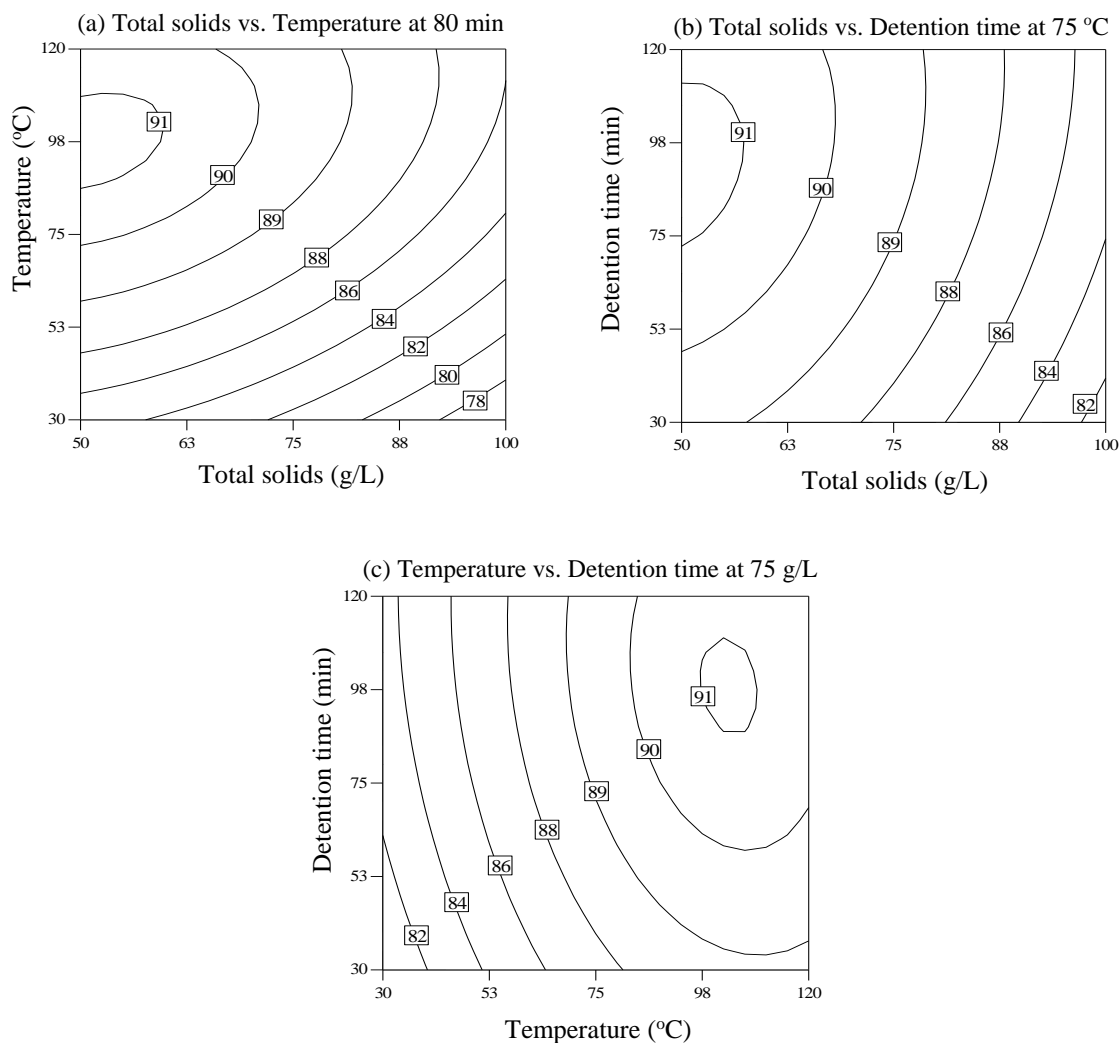
Fig. 4.3 Two-dimensional contours plots of K removal (%) as a function of (a) total solids (g/L) vs. temperature (°C), (b) total solids (g/L) vs. detention time (min), and (c) temperature (°C) vs. detention time (min).

4.4. Quantitative potassium by energy dispersive X-ray

The fibers specimens from group of raw EFB and treated EFB fibers by hydrothermal treatment (condition: 50 g/L at 120 °C for 120 min) were randomly picked for cross section view by scanning electron microscope (SEM) (images not show) prior to detect potassium (% dry wt) by energy dispersive x-ray (EDX). The quantitative K of these two EFB fiber samples were tested from

the surface till the core fiber with the estimated distance (µm). Without using any treatment, the raw EFB fiber clearly has higher in amount of K compared to treated EFB at each distance from the surface to core fiber, respectively (Fig. 4.4). This may refer that hydrothermal treatment increased the size of EFB pores and also the accessible EFB surface area while exposing cellulose structure, opening up more spaces, and removing the interfiber materials from its main fiber (Palamae et al., 2017; Sung et al., 2010) and improved the K content removal. The lowest K contents are 0.50 and 2.70 % dry wt from surface to the first layer (75.0 and 55.7 µm) while 4.20 and 5.50 % dry wt from surface to the core fiber (224.5 and 302.4 µm) of the raw and treated EFBs, respectively; so the more nearer of distance to the surface, the less potassium found. Potassium substance locates everywhere at each layer of EFB. But the K content mostly restrains in its core fiber is the new interesting finding to get known from this research. On the other hand, the different K content in EFB by EDX and ICP-OES (Table 3.1, 20,467 mg/kg which is ~ 2.10 % dry wt) may be caused by sample selection and analytical techniques since only one fiber from the EFB fibers sample was picked randomly for EDX while a batch of EFB fibers were picked and homogenized prior for analysis with ICP-OES.
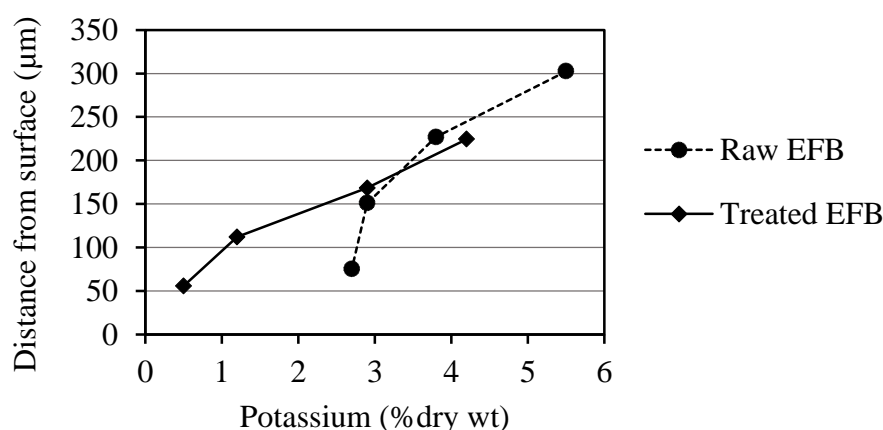

Fig. 4.4 Quantitative potassium (%dry wt) of the raw EFB and treated EFB from surface to core fiber by EDX.

4.5. Potential total oil recovery

A number of the literatures reported that oil moves to the surface of EFB fiber either by stripping or threshing process (Abd Majid et al., 2012; Md Yunos et al., 2017a) during oil mill processing. Total oil may include crude oil, free fatty acid and fatty acid constituents (Md Yunos et al., 2017a); which is economical, useful as biodiesel resultant and for daily consumption. And the approximate price for oil is about 22.9 THB per kg (Colchester et al., 2011). Thus, EFB fiber sample is still economical significant for its oil recovery for many research fields. In this research, the potential oil recovery (%) from EFB fiber samples treated at lowest and highest temperature (30 and 120 ^{o}C) for shortest and longest detention time (30 and 120 min) under lowest and highest total solids concentrations (50 and 100 g/L) shows in Table 4.2 Yield of the potential total oil recovery was enhanced by increasing temperature and detention time for both TS, respectively. The minimum total oil was recovered by ambient temperature treatment (30 ^{o}C temperature) at 64.4 ± 2.30 for 30 min detention time and 72.0 ± 1.20 for 120 min detention time under 50 g/L TS. At hydrothermal treatment of 120 ^{o}C temperature, the maximum total oil was resulted in the value of about 92 % for longest 120 min detention time under both TS concentration. From the literature, it was said that the elevated temperature can improve oil solubility and diffusion while lowering the oil viscosity (Perez et al., 2011; Tunio et al., 2011). Potassium removal (%) was maximized at lower TS, in opposite much TS utilization was yielded in higher potential total oil recovery than less TS according to the experimental data from this study.

Table 4.2 Yield of potential total oil recovery (%) under TS of 50 g/L and 100 g/L.

Temperature (°C)	Detention time (min)	Initial total oil (g/kg)	Potential total oil recovery (%)	
			50 g/L TS	100 g/L TS
30	30	49.1	64.4 ± 2.30	71.8 ± 1.90
	120		72.0 ± 1.20	74.7 ± 1.20
120	30	49.1	86.4 ± 0.40	91.7 ± 2.60
	120		92.1 ± 0.90	92.1 ± 1.50

4.6. Mass balance

The mass balance is a necessary detail for the experimental operation and technology selection as well as the cost estimation. The parameters such as VS, ash, K, total oil, SI, and FI were determined following the methods in section 3.4. The raw fresh EFB contains much moisture of 581 kg/ton EFB$_{wet}$ (~ 58 % wt) while TS is 419 kg/ton EFBwet. This is in agreement with Mohammed et al., 2012 and Luk et al., 2013, who reported that raw EFB contains high moisture content about 50-60 % wt. The total MC of 545 kg was lost from EFB after sun drying process. The MC of 9.60 kg and TS of 111 kg after cutting (plus sieving), 2.00 kg as solid particle in liquid (leachate) after hydrothermal treatment with lab-scale autoclave facility, 1.00 kg as solid particle in leachate after spinning, and 1,188 kg as moisture after drying at (103 °C) were respectively lost. For this study, total solids (TS) loss by cutting process was found very high which may cause by mechanical force utilization on EFB fiber samples, plus the manual sieving was able to remove undesired elements and solid particle from EFB samples.

In comparison to raw TS in fresh EFB, TS was lost in the amount of 114 kg (305 kg remaining) after passing by many processes which is equivalent to about 27.2 % loss at the end of process flows. At the last of processes, the EFB sample was also analyzed for its characteristics (mainly ash, K, total oil, SI, and FI), respectively (Fig. 4.5). According to processes, it shows high significant for

ash, K, SI, FI, and particularly total oil; providing high quality fuel of EFB prior for the combustion. In this study, potential total oil for each process can't be calculated because there are unknown values of potential total oil to the leachate after hydrothermal treatment with autoclave and spinning. But some amounts of potential total oil are assumed to be lost at these both processes.
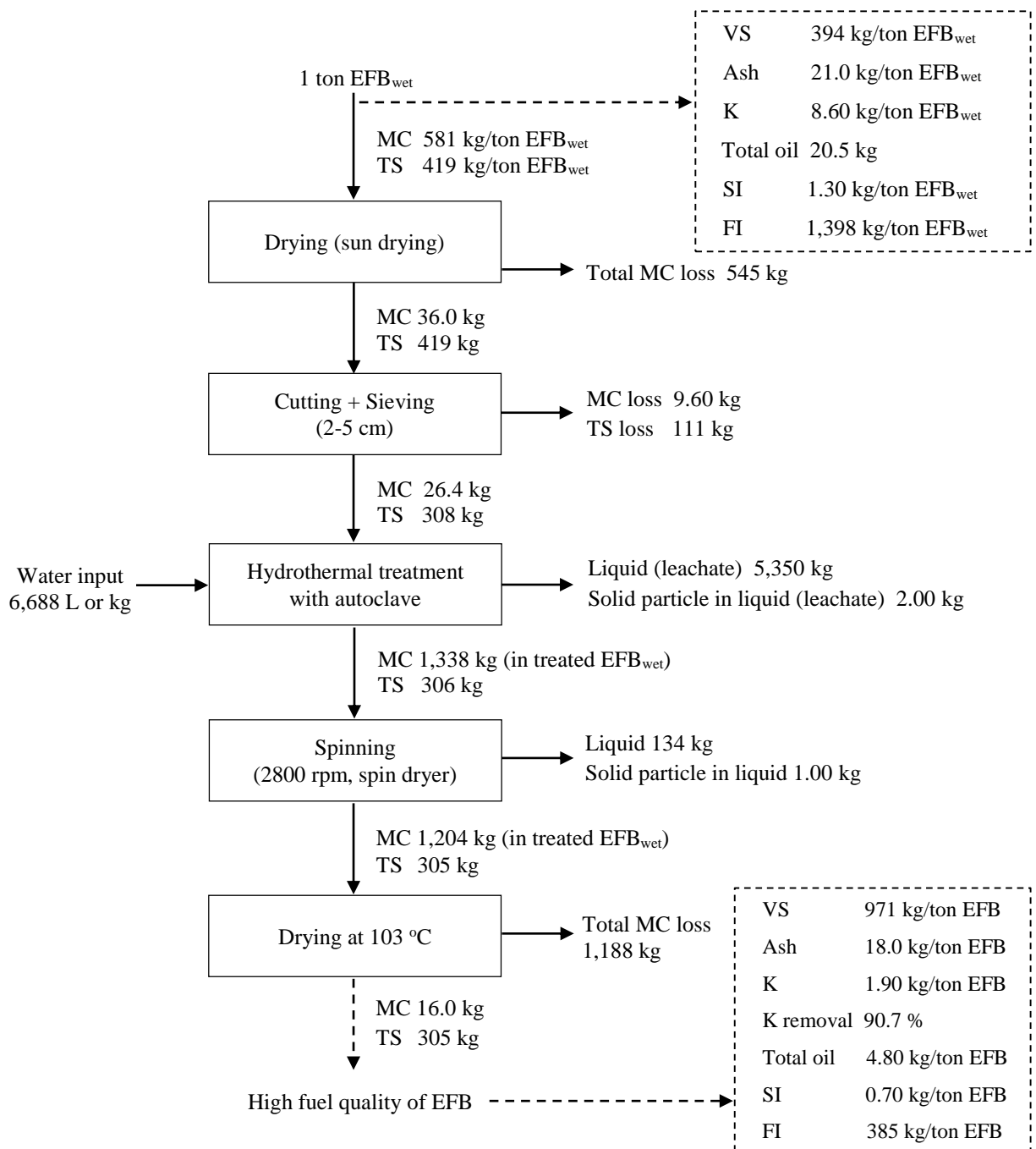

Fig. 4.5 Mass balance from 1 ton EFB$_{wet}$ to final 103°C drying process.

CHAPTER 5

CONCLUSION AND SUGGESTIONS

5.1. Conclusion

In this work, hydrothermal treatment at higher temperature and longer detention time under lower total solids impacted positively for EFB biomass property improvement in reason that over 90 % of potassium was removed from EFB at 120 ºC for 120 min under 50 g/L following by ambient temperature treatment batch. Also, the optimum total oil recovery (%) was highly yielded of about 92 % at this optimum treatment condition.

The remaining K has inverse sufficient correlation with SI and FI, which expressed by high coefficients R^2 between remaining K (%) vs. SI (% dry wt) and remaining K (%) vs. FI (% dry wt). Furthermore, the regression models from full factorial design greatly proved the adequate significance ($p < 0.0001$) on K removal from treatments in the relation to three independent variables (temperature, detention time, and total solids). Hence, this shows the main point concerning K removal (%) from the EFB biomass to the reduction in SI and FI from its EFB ash as the proof of the treating effectiveness.

The EDX analysis affirmed that K clearly contains much in the more inner layer of EFB (core fiber). The K location is also a new attempt found from this study. Total solids from raw TS/ton EFB_{wet} was lost through drying (sun drying), cutting (plus sieving), treating with autoclave (120 ºC, 120 min), spinning (2800 rpm), and drying (103 ºC); and it took with satisfactory removal and reduction of harmful K and SI and FI.

Hydrothermal treatment is a promising technique to improve EFB biomass quality in terms of potential inorganic K removal and also SI and FI reduction. This treatment technique is economical due to the low reaction temperature requirement or low energy input (low temperature). The removal

and reduction of these unfavorable elements give noteworthy benefit for the clean combustion power plant and rise of productivity in term of less ash deposits, less maintenance, much heat transfer improvement, and smooth production process. Nevertheless, the higher temperature used for K removal might be also recommended at higher than 120 °C, i.e. 150, 180, 200, and 220 °C, since these treatment temperatures are predicted to be high enough for removal of K and other inorganics. The improved EFB could function as resource for renewable chemical production and fertilizer. Moreover, the treated EFB can be expecting to be beneficial and potential for local power plants by providing them a stepping stone to push forwards commercialization if decent treatment will be applying.

5.2. Suggestions for future work

There are some suggestions for future work that may include:

1. Higher temperature to treat EFB should held since 120 °C can remove mostly 91 % of particular inorganic potassium from EFB. However, low treatment temperature (30 to ≤ 100 °C) should be also carried out with more various TS loading to water ratio (g/L) and detention time on potassium removal because it is easy to perform, economical, and somehow it is capable for potassium removal as well (either washing or soaking).

2. There should be different types of biomasses as studied materials on potassium removal by hydrothermal treatment in reasons of thermal treatment effectiveness comparison and residual biomass wastes reduction from field when they come to be useful.

3. Other pretreatment or treatment methods like biochemical treatment should be applied since it might provide both high potassium removal and biogas production from EFB.

4.   Oil species or fatty acids of total oil from EFB should be analysed in order to investigate those different species and their benefits.

5.   Liquid fraction from the treatment should be determined for the other parameters such as sugars, COD, and phenolics for other further research purposes, which are the potential by-products leached out of EFB. At palm industry, liquid waste water from treatment will be discharging in to biogas system in order to produce biogas as the energy.

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APPEXDEX

A. Photographs for chapter 3

Fig. 1 Drying palm empty fruit bunch.

Fig. 2 Shredding palm empty fruit bunch into 2-5 cm.

Fig. 3 Brief process of hydrothermal treatment to final dried EFB sample.

B. Data for chapter 4

Table 1 Raw data of remaining potassium concentration (mg/kg) of Fig. 4.1.

Total solids (g/L)	Temperature (°C)	Detention time (min)	Average	SD
50 g//L	30 °C	30 min	3,584	22.1
		60 min	3,016	96.9
		120 min	2,750	132
	60 °C	30 min	2,428	145
		60 min	2,371	15.5
		120 min	2,271	262
	120 °C	30 min	1,952	432
		60 min	19,18	430
		120 min	1,910	14.4
75 g/L	30 °C	30 min	3,804	45.3
		60 min	3,786	103
		120 min	3,597	230
	60 °C	30 min	2,737	194
		60 min	2,656	455
		120 min	2,489	14.7
	120 °C	30 min	2,354	150
		60 min	2,342	138
		120 min	2,301	210
100 g/L	30 °C	30 min	5,523	471
		60 min	4,740	272
		120 min	4,653	287
	60 °C	30 min	4,161	110
		60 min	3,796	450
		120 min	3,404	681
	120 °C	30 min	3,036	514
		60 min	2,706	354
		120 min	2,468	173

Table 2 Raw data of remaining K (%), SI (% dry wt), and FI (% dry wt) of Fig. 4.2 (a) and Fig. 4.2 (b), respectively.

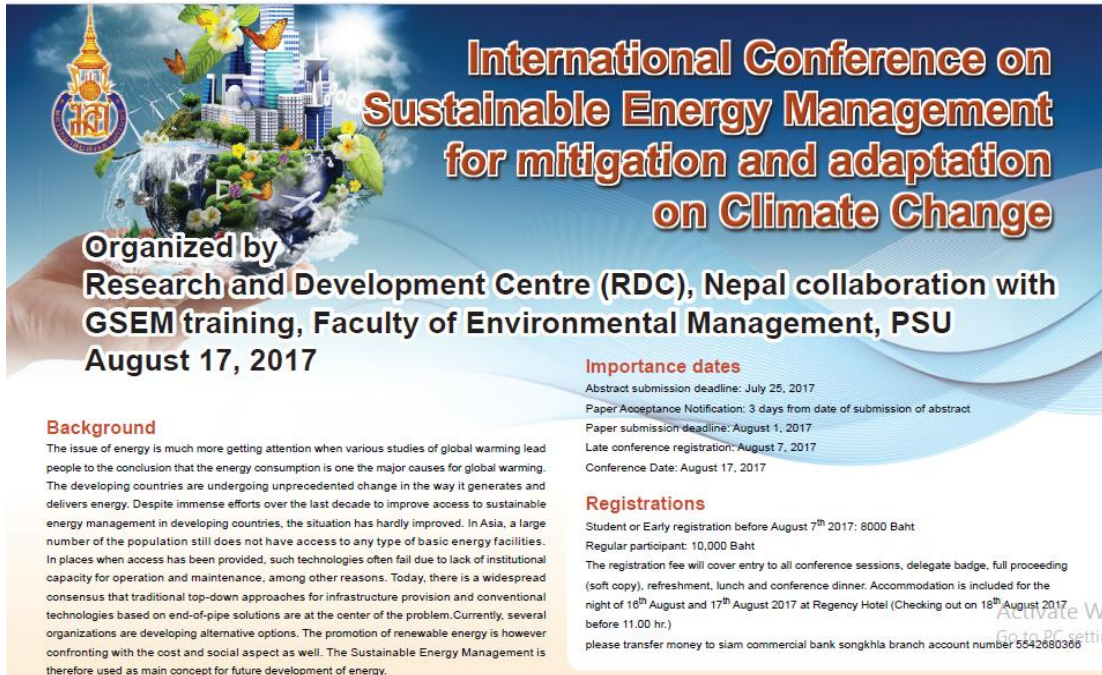| Total solids (g/L)	Temperature (°C)	Detention time (min)	Average	SD	Average	SD	Average	SD
50 g/L	30 °C	30 min	17.5	1.90	0.10	0.01	54.2	1.00
	30 °C	120 min	13.4	0.60	0.09	0.01	50.9	1.10
	60 °C	60 min	11.6	2.70	0.09	0.01	47.5	2.20
	120 °C	30 min	9.50	2.10	0.08	0.01	43.4	1.20
	120 °C	120 min	9.30	0.10	0.07	0.01	38.5	0.60
75 g/L	30 °C	60 min	18.5	0.50	0.09	0.01	54.6	0.30
	60 °C	30 min	13.4	0.90	0.08	0.01	50.1	0.30
	60 °C	60 min	13.0	2.20	0.08	0.01	49.7	0.01
	60 °C	120 min	12.2	0.10	0.08	0.01	48.8	0.80
	120 °C	60 min	11.4	0.00	0.08	0.01	47.2	0.50
100 g/L	30 °C	30 min	27.0	3.60	0.12	0.01	86.3	0.20
	30 °C	120 min	22.7	2.00	0.10	0.01	72.8	0.10
	60 °C	60 min	18.5	3.10	0.10	0.01	70.0	0.80
	120 °C	30 min	14.5	2.50	0.09	0.01	66.2	2.10
	120 °C	120 min	12.1	0.00	0.07	0.01	43.6	0.70

Table 3 Raw data of potassium removal (%) of Fig. 4.3.

Total solids (g/L)	Temperature (°C)	Detention time (min)	Average	SD
50 g//L	30 °C	30 min	82.5	1.90
		60 min	85.3	0.50
		120 min	86.6	0.60
	60 °C	30 min	88.1	0.70
		60 min	88.4	2.70
		120 min	88.9	0.00
	120 °C	30 min	90.5	2.10
		60 min	90.6	5.00
		120 min	90.7	0.10
75 g/L	30 °C	30 min	81.4	0.00
		60 min	81.5	0.50
		120 min	82.4	1.10
	60 °C	30 min	86.6	0.90
		60 min	87.0	2.20
		120 min	87.8	0.10
	120 °C	30 min	88.5	0.70
		60 min	88.6	0.00
		120 min	88.8	1.00
100 g/L	30 °C	30 min	73.0	3.60
		60 min	76.8	1.90
		120 min	77.3	2.00
	60 °C	30 min	79.7	0.80
		60 min	81.5	3.10
		120 min	83.4	3.60
	120 °C	30 min	85.2	2.50
		60 min	86.8	2.40
		120 min	87.9	0.00

Table 4 Raw data of quantitative potassium (% dry wt) by EDX of Fig. 4.4.

Sample	Distance from surface to core fiber (µm)		Potassium (% dry wt)
	0-L1	75.0	2.70
Raw EFB fiber	0-L2	150.9	2.90
	0-L3	226.9	3.80
	0-CF	302.4	5.50
	0-L1	55.7	0.50
Treated EFB	0-L2	112.0	1.20
(50 g/L at 120 ºC for120 min)	0-L3	168.5	2.90
	0-CF	224.5	4.20

C. Conference

International Conference on Sustainable Energy Management for mitigation and adaptation on Climate Change

Organized by Research and Development Centre (RDC), Nepal collaboration with GSEM training, Faculty of Environmental Management, PSU

August 17, 2017

Background

The issue of energy is much more getting attention when various studies of global warming lead people to the conclusion that the energy consumption is one the major causes for global warming. The developing countries are undergoing unprecedented change in the way it generates and delivers energy. Despite immense efforts over the last decade to improve access to sustainable energy management in developing countries, the situation has hardly improved. In Asia, a large number of the population still does not have access to any type of basic energy facilities. In places when access has been provided, such technologies often fail due to lack of institutional capacity for operation and maintenance, among other reasons. Today, there is a widespread consensus that traditional top-down approaches for infrastructure provision and conventional technologies based on end-of-pipe solutions are at the center of the problem. Currently, several organizations are developing alternative options. The promotion of renewable energy is however confronting with the cost and social aspect as well. The Sustainable Energy Management is therefore used as main concept for future development of energy.

Importance dates

Abstract submission deadline: July 25, 2017
Paper Acceptance Notification: 3 days from date of submission of abstract
Paper submission deadline: August 1, 2017
Late conference registration: August 7, 2017
Conference Date: August 17, 2017

Registrations

Student or Early registration before August 7th 2017: 8000 Baht
Regular participant: 10,000 Baht
The registration fee will cover entry to all conference sessions, delegate badge, full proceeding (soft copy), refreshment, lunch and conference dinner. Accommodation is included for the night of 16th August and 17th August 2017 at Regency Hotel (Checking out on 18th August 2017 before 11.00 hr.)
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17th August 2017

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Paper ID: A3

Effects of Hydrothermal Treatment on Palm Empty Fruit Bunch Properties

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ABSTRACT

Palm empty fruit bunch (EFB) is a waste from palm oil mills with gigantic availability in many tropical countries. Obstacle for utilizing EFB as solid fuel lies in its high potassium (K) in its biomass. In this work, EFB properties were investigated using hydrothermal treatment (HTT) aiming to remove K, which is a main inorganic substance causing slag in EFB boiler. EFB was treated in liquid at 60 and 120 $^{\circ}$C for detention time of 30, 60, and 120 min under two concentrations of total solid (TS) in water (50 and 100 gTS/L). In a control set, passing water (0 min treatment) at temperature (30 $^{\circ}$C) resulted in K removals of 49.5±0.2 and 45.1±1.1 % for 50 gTS/L and 100 gTS/L, respectively. However, K removal was enhanced to 90.7±0.1 and 87.9±0.0 % at 120 $^{\circ}$C for 120 min for 50 gTS/L and 100 gTS/L, respectively. At the selected HTT temperature of 120 $^{\circ}$C, holocellulose and ash contents in EFB were reduced with longer detention time due the enhanced inorganic release from the biomass. Increasing temperature and time while lowering TS concentration of EFB positively contributed to the improved K removal. This high potassium removal leads the reduction of fouling and slagging of K heat exchanger surface in combustion chamber which promote higher efficiency of power generation.

Keywords: Palm empty fruit bunch, Potassium, Hydrothermal treatment, Temperature, Leaching

INTRODUCTION

In Thailand, oil palm plant has been annually increasing due to the needs of its derived palm oil products for local consumption and exportation. Palm oil might be the most beneficial oil compared to other agricultural and vegetable oils (soybean, peanut, sunflower, and rapeseed oils) because of its versatility in uses as an important component in chemical, food, and biodiesel industries (Colchester et al., 2011; Barison, 2007; FAOSTAT, 2013a; Schmidt, 2015). This fact pushes massive growth of this economic crop and at the same time generates large amount of palm empty fruit bunch (EFB) as waste. This EFB biomass produced in all standard palm oil mills is accounted for 24-29 % of all byproducts (Hengniran, 2011; Lecksiwilai et al., 2016; Pleanjai et al., 2004).

Palm empty fruit bunch (EFB) can directly be used as fuel in combustion system to convert to energy. Unfortunately, high potassium content in the biomass makes it difficult for combustion application since this major inorganic element develops combustion-related problems through the formation of slack in the grate floor and heat exchange surface in combustion chamber (Saritpongteeraka et al., 2015; Mohammed et al., 2012; Obernberger and Thek, 2004). It was reported that some abundant elements in biomass such as K, Si, Ca, and Cl affect the heat transfer in boiler fouling and slagging (Madhiyanon et al., 2012). The problems of slagging and fouling from alkaline element can make ash meltdown during combustion. For burning EFB, it can produce excessive slack accumulating in boilers causing frequent shutdowns, loss of efficiency, and increases the cost of maintenance for the furnace (ISTA, 1999).

Hydrothermal treatment (HTT) is a possible method to improve the EFB biomass into a more hydrophobic, more stable, and more lignin containing feedstock (Byrappa and Adschiri, 2007; Novianti et al., 2016). HTT influences the changes of fiber composition and also remove oil from EFB that could be of value as oil recovery in palm oil mill ((Md Yunos et al., 2017b). Since EFB structural cell will be weakened by high temperature and K ion could hypothetically dissolve and remove with water. HTT process could facilitate this reaction (Achmad et al., 2014; Sun et al., 2013) at various degrees for different conditions. In some studies, HTT of EFB had been done at temperatures above 100 ℃. However, using of the temperature at lower than and equal to 100 ℃ could save energy and more practical (Kumar et al., 2009; Nurdiawati et al., 2015).

The main objective of this study was to evaluate the effects of hydrothermal treatment on EFB properties, particularly potassium removal, at different solid to liquid concentrations, temperatures, and detention times. The other parameters including solid loss, fiber composition, ash content, and oil recovery were also reported.

METHODOLOGY

Substrate

Dry shredded EFB biomass of species Eleaeis guineensis with the size range 2-5 cm was used in this research. This sample was obtained from Chumporn Palm Oil Industry Public Co., Ltd, located in Chumporn province, Thailand. Characteristics of raw EFB were analyzed for solid content, fiber composition, and inorganic contents as shown in Table 1.

Hydrothermal treatment (HTT)

In this experiment, EFB total solids concentration (TS) of 50 and 100 g/L were prepared in 2 L stainless steel container. HTT was conducted using lab-scale autoclave (TOMY Autoclave SS-325, Japan) at low and practical temperatures of 60 and 120 $^{\circ}$C for different detention times of 30, 60, and 120 min. Ambient temperature treatment (ATT) was also carried out at room temperature of 30 $^{\circ}$C for 30, 60, and 120 min. The flash washing of EFB sample which is considered as 0 min detection time was also performed in ATT experiment as a control set. Each treatment was done in 3 replicates. At each completed treatment, muslin cloth was used in order to separate EFB and leachate (liquid fraction). Continuously, treated EFB was spun with a spin dryer at 2800 rpm for 5 min (White Knight 28009W Gravity Drain Spin Dryer, German) for moisture removal. After each completed spinning, treated EFB was collected and oven dried at 103 $^{\circ}$C till constant weight. Mainly, potassium content in treated EFB of each treatment was measured and compared to that of the raw EFB. Potassium removal (%) was then calculated.

Analytical methods

Total solid (TS), volatile solids (VS), and ash were determined using modified Laboratory Analytical Procedure (LAP001 and LAP005) developed by the National Renewable Energy Laboratory (NREL LAP, 1994). Both raw and treated EFB were dried at 103 $^{\circ}$C to a constant weight and prepared for total oil analysis by Acid Hydrolysis Method (in-house method based on AOAC Official Method 922.06, 2006). K, Ca, and Mg detection were carried out by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Optima 8000, Perkin Elmer, USA) at wavelength of 766.490, 317.933, and 285.213 nm, respectively. Furthermore, the ground sample was used to determine fiber composition by neutral detergent fiber (NDF), acid detergent fiber (ADF), and acid detergent liquid (ADL) (Goering and Van Soest, 1970; AOAC, 2006). Cellulose, hemicelluloses, and lignin percentages were resulted by AD–ADL, NDF–ADF, and ADL, respectively. Then, holocellulose can be calculated by summing up cellulose and hemicellulose. At the end of experiments, dry EFB was weighed in order to calculate solid loss based on equation 1.

$$\text{Solid loss (\%)} = \frac{\text{Initial Weight} - \text{Remaining Weight}}{\text{Initial Weight}} \times 100 \qquad \text{(Eq.1)}$$

RESULTS AND DISCUSSIONS

Substrate characteristics

Some major components of raw EFB are shown in Table 1. EFB is composed of cellulose, hemicellulose, and lignin at 47.7±0.8, 20.2±1.0, and 10.5±0.4 % dry wt, respectively, while ash content in the raw EFB was found at 5.2±0.2 %dry wt which is consistent with other reports at 5.4 and 5.9 %dry wt (Geng, 2013; (Mulyantara et al., 2017)). Potassium (K), the main inorganic, was found at 2.1 %dry wt which is higher than other inorganic elements such as Ca and Mg (Table 1). Previous studies reported that K in EFB amounts for 2.0-2.2 %dry wt (Geng, 2013; Abdullah et al., 2011). High K content in EFB is a major cause of slagging and fouling in EFB-based biomass power plant.

Table 1. Characteristics of the raw EFB.

Parameter	Raw EFB
Proximate analysis	
Volatile solids, VS (g/kg dry)	948.5±2.2
Ash (%dry wt.)	5.2±0.2
Total oil (%dry wt.)	4.9±0.2
Fiber composition	
Cellulose (%dry wt.)	47.7±0.8
Hemicellulose (%dry wt.)	20.2±1.0
Lignin (%dry wt.)	10.5±0.4
Holocellulose (%dry wt.)	67.9
Inorganic element	
Potassium, K (%dry wt.)	2.1
Calcium, Ca (%dry wt.)	0.2
Magnesium, Mg (%dry wt.)	0.1

Potassium removal efficiency

In this study, potassium removals from EFB were found affected by both ATT and HTT. Potassium removal efficiency from 50 and 100 gTS/L at 30 to 120 °C for 0 to 120 min detention time is presented in Fig. 1. By comparing K contents of treated EFB samples to raw EFB, removal efficiencies were ranging from 45.1 to 90.7 %. The washing at 30 °C (for 0 min detention time) already achieved K removal efficiency of about 50 % (Fig. 1). Potassium ion (K^+) will likely react with OH^- ion in the water; so that it can be highly solubilized by water (Achmad et al., 2014; Sun et al., 2013; Knudsen et al., 2004). Therefore, a demonstration that simple biomass washing by

distilled water at room temperature (30 °C) removes simple alkali substances which dissolve easily. In this study, it was found that low TS (50 gTS/L) gave higher K removal than 100 gTS/L at all temperature (30, 60, and 120 °C) because of lower concentration in the bulk liquid promoting higher concentration gradient between K in fiber and that in bulk liquid. K removal did not show significant different efficiency at high temperature of 120 °C for 30 to 120 min of 50 gTS/L. This might be K in fiber can release 90.5 % in the first 30 min (Fig. 1a). High TS loading (100 gTS/L) gave larger gap of K removal at different temperatures (Fig. 1b). Hence, low TS loading and long detention time at high temperature can help K release. It was reported that HTT technique is expected to support the reaction since it loosens the structure of EFB fiber and K ion would easily release and dissolved into water (Achmadet al., 2014).
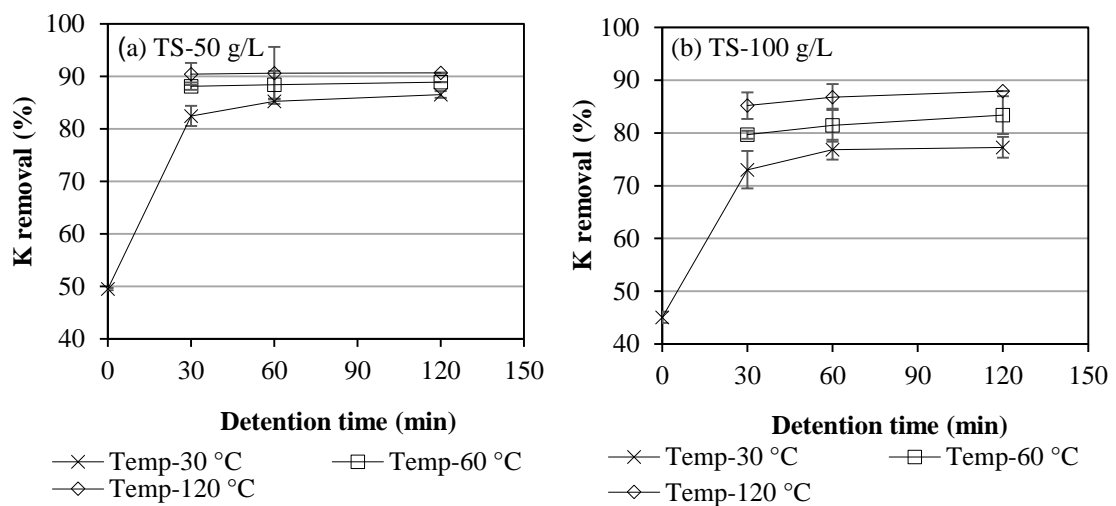
Fig. 1. K removal from treated EFB at 30 to 120 °C for 0 to 120 min of (a) TS-50 g/L and (b) TS-100 g/L.

Relationship between solid loss and potassium removal

Fig. 2 shows the correlation between solid loss (SL) and potassium removal from 50 and 100 gTS/L under temperature of 30 to 120 °C for detention time 0 to 120 min. The polynomial correlation equation of solid loss and potassium removal showed in Eq. 2 and Eq. 3 of 50 gTS/L and 100 gTS/L as follows.

50 gTS/L   : K removal = -0.1232 SL^2 + 6.7811 SL   R² = 0.9919   (Eq. 2)

100 gTS/L : K removal = -0.1701 SL2 + 7.6235 SL   R² = 0.9461   (Eq. 3)

HTT could affect solid loss of EFB and leads to COD increment (data not shown) because of HTT can partially break down fiber structure. Therefore, the inorganic elements and minerals were dissolved to liquid fraction. Potassium is mainly lost by liquid leaching and the more crumbled the structure, the easier K ion could leave the structure (Reza et al., 2013; Pisupati and Bhalla, 2008). Solid loss increased with the increasing temperature and detention time (Fig. 2).
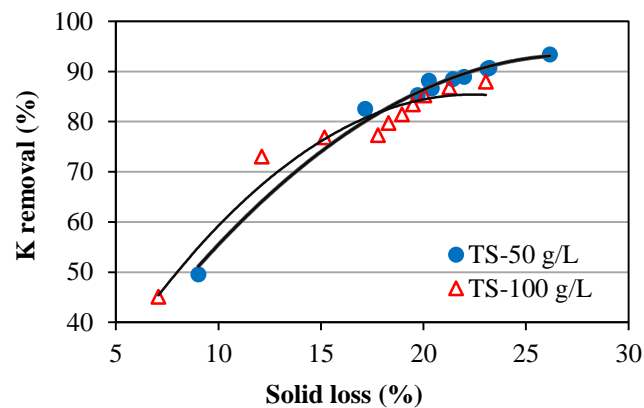

Fig. 2. K removal and solid loss correlation at 30 to 120 ºC for 0 to 120 min of TS- 50 g/L and TS-100 g/L.

Fiber composition

EFB fiber composition before and after HTT are showed in Fig. 3. Lignin and holocellulose increased when temperature and detention times were increased. There is no significant change of lignin as it remains rather stable around 12 %dry wt at both 50 and 100 gTS/L. It was earlier reported that lignin dissolves at higher temperature range of 140 to 260 °C (Reza et al., 2013; Smith et al., 2016; Nomanbhay et al., 2103; Libra et al., 2011). Thus, the lower temperature (30-120 ºC) used in this study is not sufficient for lignin dissolution. Thermal autoclaving caused little change in lignocellulose; thus reaffirming the idea that this treatment was not severe enough to reduce lignin (Cao et al., 2012b) but could sufficiently remove K from the fiber. It was also found that ash content slightly decreased from 1.6 %dry wt (or 69.3% removal) to 1.4 %dry wt (or 72.0 % removal) for 50 gTS/L and from 1.7 %dry wt (or 66.6 % removal) to 1.5 %dry wt (70.1 % removal) for 100 gTS/L, respectively (Fig. 4). This shows a positive impact of HTT to decrease ash and K simultaneously.
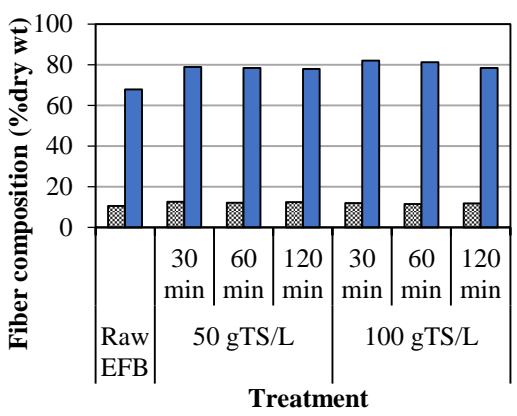
Fig. 3. Fiber composition of raw EFB and treated EFB at 120 °C.
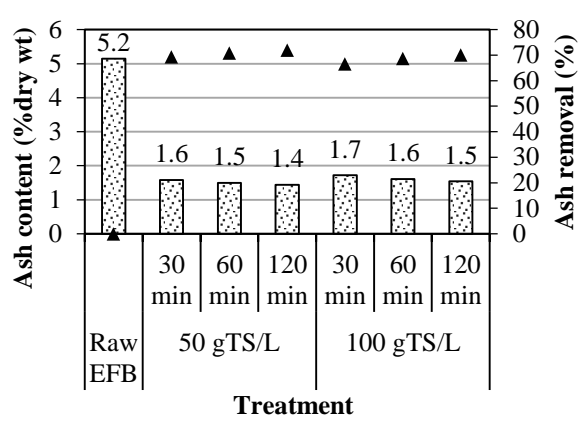

Fig. 4. Ash content and ash removal of raw EFB and treated EFB at 120 °C.

Oil recovery

Potential oil recovery expressed as the percentage of oil extracted from the fiber. This term is represented by the change of oil content in fiber before and after HTT. According to the results, oil recovery was increased by increasing temperature sand detention times (Fig. 5c and 5d). Total oil recovery from EFB could be higher than 60 % at only 30 °C for 30 min and the highest was over 90 % at 120 °C for 120 min detention time for both TS concentrations. It was notice that lower TS of 50 g/L gave slightly higher oil recovery. The elevated temperature can enhance oil solubility and diffusion while lowering the oil viscosity (Tunio et al., 2011; Perez et al., 2011).
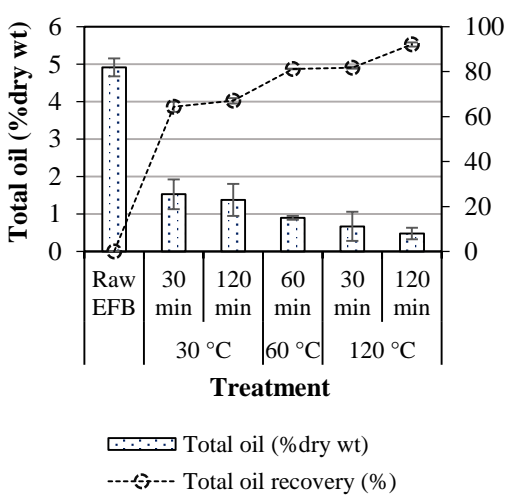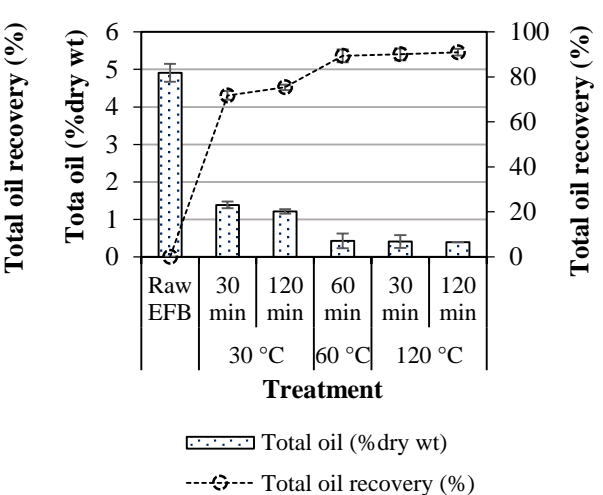
Fig. 5. Total oil and total oil recovery from (c) TS-50 g/L and (d) TS-100 g/L at selected temperatures and times by response surface method (RSM).

Conclusion

Hydrothermal treatment is a promising technique to improve EFB biomass quality in terms of major inorganic potassium removal. This process is economical due to the low temperature requirement or low energy input. Hydrothermal treatment at higher temperature and longer time impact positively for biomass properties improvement. Over 90 % of potassium was removed from EFB at 120 °C for 120 min. Further analysis of reduction in slagging and fouling indices of the EFB ash will be carried out to confirm the effectiveness of this strategy in combustion chamber of EFB biomass power plant.

Acknowledgements

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TAN, C., Saritpongteeraka, K., Kungsanant, S., Charnnok, B., Chaiprapat, S., 2017. Effects of Hydrothermal Treatment on Palm Empty Fruit Bunch Properties. International Conference on Sustainable Energy Management for Climate Change Adaptation and Mitigation. 17th August 2017, Siam Oriental Hotel, Hat Yai, Songkhla, Thailand.