



Review Article: Appropriate Hydrothermal Pretreatment of Oil Palm Biomass in Palm Oil Mill

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Abstract – Oil palm (*Elaeis guineensis* Jacq.) is one of the most planted trees in Malaysia for the palm oil production. Thus, solid biomass had been generated from this industry such as empty fruit bunch, shell, mesocarp fibre, frond and trunk produced that causes problematic to the nation and expected to escalate up to 85-110 million tonnes by 2020. Besides that, palm oil mill effluent and excessive steam also generated from the production of palm oil. *In situ* hydrothermal pretreatment means the utilisation of excessive steam produced by the oil palm mill and at the same time, generating value added product as well as reducing the biomass. Oil palm biomass is rich in lignocellulosic materials which comprised of lignin, hemicellulose and cellulose. Refinement of lignocellulosic from oil palm biomass can be utilised to form fermentable sugar, bioethanol and other potential chemicals. Recalcitrant property of lignocellulosic reduces the ability of enzymes to penetrate, thus pretreatment is required prior to hydrolysis process. Pretreatment can be either physical, chemical, biological or combined. In this review paper, three types of hydrothermal pretreatment were discussed as suitable *in situ* pretreatment process for oil palm biomass; in palm oil mill. The suitability was measured based on the availability of excess steam and energy in the mill. Furthermore, physicochemical pretreatment also facilitate the saccharification process, whereby it loosened the lignocellulose structure and increase the surface area. The effects and factors in choosing right pretreatment are highlighted in this paper.

Keywords: *Elaeis guineensis*, oil palm biomass, hydrothermal, pretreatment, lignocellulose

Introduction

Oil palm is planted in 43 developing countries that are in tropical climate, and currently making Malaysia as one of largest palm oil producers. The seed was originally transported from Africa, and Malaysia currently produced 19.67 million tonnes per year of crude palm oil which resulting 100.4 million metric tonnes annually of fresh fruit bunch is collected to be processed (Ibrahim et al., 2017). Thus, creating large amount of oil palm biomass such as oil palm empty fruit bunch (OPEFB), oil palm mesocarp fibre (OPMF) and oil palm fronds (OPF), oil palm trunks (OPT) that contributed to cumulatively of 40-50 million tonnes per year (Abdullah et al., 2016; Kabbashi et al., 2007). OPEFB was generated from oil palm mill in the process of sorting, sterilization and threshing process. The oil palm fruits were sorted according to the maturity of the fruit, and then continued to sterilization process. In this step, the fruits were sterilized to inactivate the enzymes that can affect the crude palm oil (CPO) quality, thus enhancing the threshing process. After threshing process, empty fruit bunch was separated

and shredded, continued to incineration, and then the ash was collected for fertilizer amendment (MPOB, 2008). However, the incineration procedure is discouraged due to pollution effect, thus the OPEFB is returned to the plantation and act as mulch to the soil. Meanwhile, OPMF is generated through palm oil processing and comprised of crushed endocarp, mesocarp and exocarp (Zakaria et al., 2014b). There are three parts of OPF which have been recognized, only the basal part is taken due to high cellulosic materials which then contributes to production of sugar, while the top and middle part are left at plantation to avoid soil erosion, leaching and runoff (AIM, 2011). Throughout years, amount of each biomass increased and expected to have 85-110 million tonnes by 2020 (AIM, 2011). Biomass production can be beneficial through complete utilization (Li et al., 2007). Oil palm trunks biomass is obtained only at the end of plantation period when the trees are unable to produce good quality of oil palm fruits. All of these biomass contained lignocellulosic materials which are lignin, hemicellulose and cellulose (Hashim et al., 2011; Kabbashi et al., 2007; Mohammad et al., 2012). Lignocellulosic materials bounded together with different approaches which lignin is associated chemically and physically with cellulose, while hemicellulose is associated physically only with cellulose. Therefore, lignin is bounded tighter and required pretreatment process in order to loosen up the structure (Mosier et al., 2005).

There were several types of pretreatment that are biological, physical, chemical, and combined like physicochemical pretreatment. Biological pretreatment involving enzymes, microorganisms including bacteria and fungi. Example of biological pretreatment of empty fruit bunch by Isroi et al. (2012), white-rot fungi, *Pleurotus floridanus* was used to break down lignin and alter lignocellulosic structures. Ligninolytic enzymes produced from white-rot fungi efficiently degrading the lignin and also capable to degrade holocellulose, thus lowering the cellulose crystallinity. Meanwhile, physical pretreatment uses thermal reaction such as pyrolysis, and mechanical comminution using grinder, miller or chipping timber in order to reduce the size of biomass structure. Disruption of lignocellulosic structure and increasing the surface area to enhance enzymatic hydrolysis (Zakaria et al., 2014a). Disadvantage of using biological pretreatment was the microorganism should be viable in order to react with substrates, while physical pretreatment involved additional power used of electrical appliances such as disk milling. Chemical pretreatment such as formiline had shown effective results which lignin and hemicellulose were removed and contributed to more than 90% of polysaccharides conversion (Cui et al., 2014). Introducing chemical in pretreatment process leads to chemical reaction and causing the internal parts of biomass changing; hence loosen the structure. The usage of chemical is not environmental friendly and can cause pollution after the pretreatment process. Physicochemical pretreatment changes both external and internal structure of biomass for example steam explosion, hydrothermal pretreatment and hot compressed water. In this paper, hydrothermal pretreatment is the main concern; therefore only physicochemical reaction will be highlighted.

Lignocellulosic material

Jacobsen and Wyman (2000) stated that lignocellulosic biomass comprises three major fractions- cellulose, hemicellulose, and lignin with the presence of minerals such as ash and extractives. Cellulose comprises 35%-50% of the total dry mass and linked by β -1,4-glucoside bonds that contributed to long chains of β -anhydroglucose units. Cellulose in lignocellulosic materials is bound laterally about 50%-90% of hydrogen bonds, thus, crystalline structure formed. The remaining portion is called amorphous cellulose are less ordered. Crystallinity of cellulose becomes a major challenge in effective hydrolysis. The surface area of the biomass, available to the cellulase enzyme can be considered as the rate of enzymatic hydrolysis. Enzymatic hydrolysis rate could be reduced in the presence of hemicellulose and lignin due to physical contact towards cellulose. From total lignocellulosic mass, 29% are made up of hemicellulose and the hemicellulose monomer unit can be fermented to ethanol same as cellulose (Ray

and Sain, 2017). Hemicellulose comprised of branched sugar chains of mainly aldopentoses, such as xylose and arabinose, and some aldohexoses, such as glucose, mannose, and galactose. In addition, a hemicellulose polymer has high degree of depolymerisation because of substituents on the main chain or its branches. Within the structure of biomass, hemicellulose is linked with cellulose and lignin by covalent bonds, thus, hemicellulose can be broken down easier than crystalline cellulose. However, the heterogeneity of hemicellulose leads to difficulties in understanding the process of hydrolysis and resulting variation of hydrolysis reaction mechanisms unlike homogeneity of cellulose. Lignin can be degraded into three main monomers of lignin are syringyl (S), guaiacyl (G) and 4-hydroxyphenyl (H) (Gao et al., 2017). Cellulosic fibers could be attached by lignin as it acts as natural glue or reinforcing material which can bind the lignocellulosic material together and make lignin water insoluble material and (Ali et al., 2015; Govender et al., 2009; Zhu et al., 2010). Degradation of lignocellulosic materials can be determined into various potential products as shown in Figure 1.

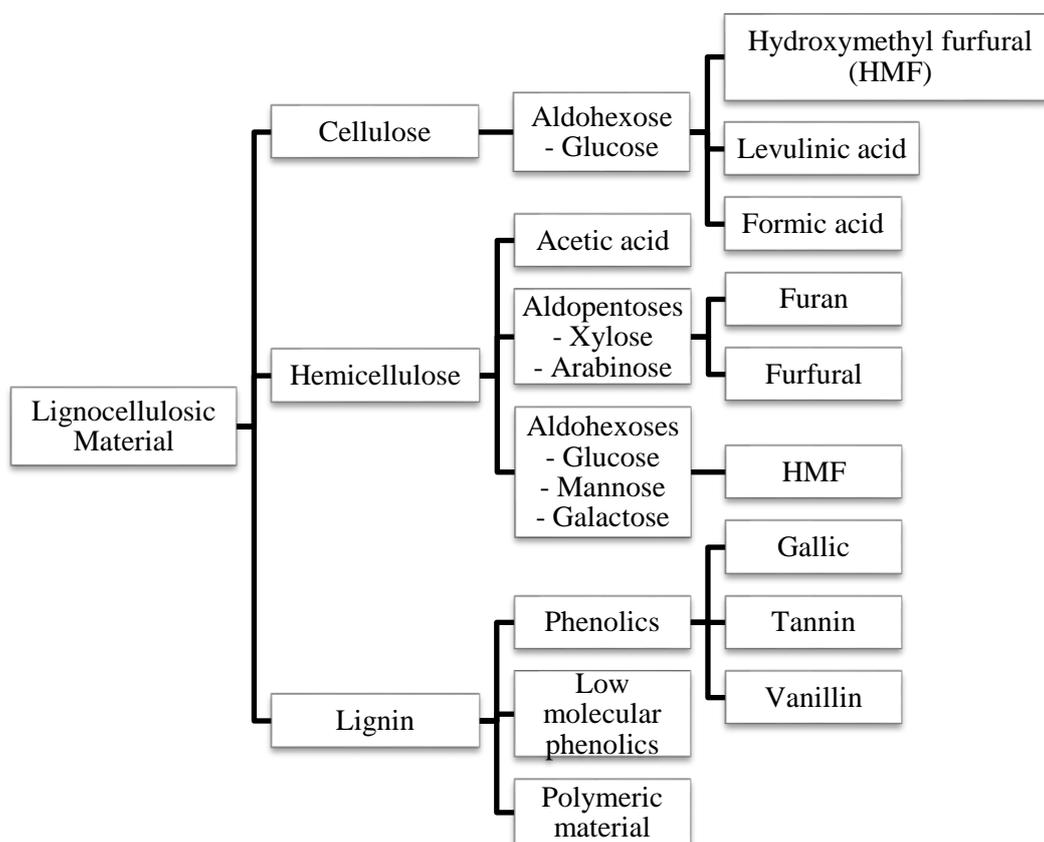


Figure 1: Potential degradation products of lignocellulosic component (adapted from Demirbas, 2007; Jacobsen and Wyman, 2000; Mosier et al., 2005; Zakaria et al., 2016)

Importance of cellulose

Cellulose is the most renewable natural resource on Earth as it existed in most of the living organisms and can be source of carbon source that can solve the diminishing of fossil fuel problems. Based on previous research (Goh et al., 2010), limitation of energy becomes a worry towards human kinds and civilization. Even though revolution of industrial has transformed the world into urbanization edge, there are still main reliant on fossil fuels for the energy source. Towards the end, fossil fuels will diminished due to non-renewable property. In addition, petroleum-derived fuels demand is keep increasing for over the past few years including Malaysia for 44,268 ktOE in the year 2007 (Goh et al., 2010). Besides that, it will lead to global warming as the fossil fuel diminishing.

Edible source can be converted into bioethanol and known as first-generation bioethanol (FGB). However, the FGB gives drawbacks since it produced from corns and sugarcane. Due to this circumstance, second-generation bioethanol (SGB) offers greater impact as they are derived from non-edible sources such as lignocellulose biomass, which comprises mainly of cellulose, hemicellulose and lignin to replace fossil fuels. A production of mixture of pentoses (C₅) and hexoses (C₆) can be produced from the hydrolysis of long chain of lignocellulosic polymers which can be further converted to ethanol.

Goals of pretreatment

Recalcitrance of lignocellulosic material such as cellulose crystallinity, restricted surface area due to cellulose covered by lignin and sheathed by hemicellulose, dissimilarity character of particles such as tenderness, limit the enzyme attack; therefore high loading of enzyme is required to have an effective hydrolysis (Mosier et al., 2005). However, higher cost might be incurred by the usage of enzyme loading compared to product market value. Therefore, pretreatment process is required as it can help in increasing the pore volume and enlarging surface area thus allowing the accessibility of cellulase into cellulose to produce monosaccharide, hence creating economic feasibility (Kim et al., 2013). Besides that, the disruption of lignin and degradation of hemicellulose leave the cellulose alone, thus cellulase can be easily attacking the cellulose. Minimizing the amount of inhibitor also had becoming the concern in choosing the right pretreatment. Examples of pretreatment process are dilute sulfuric acid treatment, lime pretreatment, steam explosion, ammonia pretreatment and hot compressed water treatment (Demirbas, 2007; Kim et al., 2013; Zakaria et al., 2015a). In pretreatment process, the affect is calculated by severity factor which explaining the results affected on substrates based on treatment temperature and time taken (Garrote et al., 1999). The severity factor can be calculated through the following equation:

$$R_0 = t \cdot \exp \left[\frac{(T-100)}{14.75} \right] \quad \text{[Equation 1]}$$

However, Equation 1 only includes water-only hydrolysis, for combined severity factor, hydrogen ion activity also can be derived into the Equation 2:

$$R_0 = [H^+] \cdot t \cdot \exp \left[\frac{(T-100)}{14.75} \right] \quad \text{[Equation 2]}$$

Where t is reaction time (min), T is hydrolysis temperature (°C) and $[H^+]$ is pH of liquor after pretreatment condition Chum (Chum et al., 1990a, 1990b) as reported in Teramoto (Teramoto et al., 2008).

Hydrothermal Pretreatment

After threshing the oil palm fruits from bunch, the fruits were undergoing sterilization process. In sterilization process, pressurized steam was used to loosen the fruits which allowed the fruits to detach from the fibrous part. Besides that, steam also helps in loosening the kernel and the shell, thus facilitating the process of nut cracking (Poku, 2002). Usually, the steam in palm oil mill is generated more than required steam, hence creating 176,925 tonnes/year of excessive steam (Abdullah et al., 2016). The excessive steam is not utilized and wasted by releasing to the environment. The energy from the steam can be reutilized for developing *in situ* hydrothermal pretreatment process (Shamsudin et al., 2012; Zakaria et al., 2015b). Hydrothermal pretreatment or also known as autohydrolysis process involving range of treatments including hot water and steam based processes (Liu, 2010).The

advantages of hydrothermal pretreatment are partially removal of hemicellulose and lignin migration thus creating greater effect of expended surface area and pore volume (Zakaria et al., 2015a). These can enhance the cellulose hydrolysis by allowing the cellulase to react. Besides that, the hydrothermal pretreatment is safe to the environment since no chemical is involved (Kumar et al., 2009). Therefore, the biomass can be utilized and in the same time the excessive steam can be used as pretreatment of biomass to increase the production of sugars where the palm oil mill can imply the concept of from waste to wealth. By implementing this concept, it will create a better environment and solution for oil palm industry.

Hot Compressed Water

Hot compressed water (HCW) pretreatment is a process that uses only water without catalyst in a closed reactor under elevated temperature and pressure (Goh et al., 2010). Hydronium ion from water ionization act as reaction medium since water dissociates when heat is applied (Table 1) (Boyd, 2015; Cushman, 2015; Jim, 2017; Sabiha-Hanim et al., 2011; Zakaria et al., 2015a). Increasing of temperature will reduce its viscosity, therefore the water molecules collide each other faster. Dissociation of water molecules resulting in increasing of hydrogen ions, H^+ in the solution (Barron et al., 2005). However, increasing temperature doesn't always make the water turns more acidic, yet the solution can turn into acidic when hydrogen ions are excess compared to hydroxide ions. Water is always having hydrogen ions and hydroxide ions equally, therefore, water still neutral even though the pH changed (Jim, 2017). HCW efficiently solubilize the hemicellulose, thus the acetyl group from hemicellulose is released and creating acidic condition by itself (Inoue et al., 2008). Based on Goh et al. (2012), OPF had been pretreated with hot compressed water under 160-200°C at 45-90 min. Their research found that glucose yield can be obtained up to 83.72% with severity factor of 3.31. In another study by Zakaria et al. (2015a) observed that shorter time can be conducted to obtain higher glucose conversion. OPF and OPEFB were subjected to hot compressed water pretreatment separately using stainless steel tube reactor heated by sand bath in range of 170 to 210°C for 10 min and 210 to 250°C for 20 min respectively with ratio of solid to liquid 1:10. In their study, the glucose conversion yield can be achieved at 87-100% after treated at high severity factors. The pore volume and specific surface area of treated samples were enhanced compared to untreated sample, thus creating better enzymatic hydrolysis. Specific surface area of OPF with $7.2 \text{ m}^2\text{g}^{-1}$ compared to $0.98 \text{ m}^2\text{g}^{-1}$ of untreated sample, whereas $5.5 \text{ m}^2\text{g}^{-1}$ of treated OPEFB contrasted with $0.98 \text{ m}^2\text{g}^{-1}$ of untreated OPEFB sample. Meanwhile, pore volume of treated OPF and OPEFB resulting $0.045 \text{ cm}^3\text{g}^{-1}$ and $0.042 \text{ cm}^3\text{g}^{-1}$ compared to $0.0072 \text{ cm}^3\text{g}^{-1}$ and $0.0056 \text{ cm}^3\text{g}^{-1}$ of untreated OPF and OPEFB, respectively. Both results were from the highest severity factor treatments. This concluded specific surface area and pore volume play important role of glucose conversion through enzymatic hydrolysis.

Table 1: Effect of water temperature towards K_w and pH value (Boyd, 2015; Jim, 2017)

Temperature of water (°C)	K_w	(H^+)	pH	pOH
0	$10^{-14.94}$	$10^{-7.47}$	7.47	7.47
5	$10^{-14.73}$	$10^{-7.36}$	7.36	7.36
10	$10^{-14.53}$	$10^{-7.26}$	7.26	7.26
15	$10^{-14.35}$	$10^{-7.18}$	7.18	7.18
20	$10^{-14.17}$	$10^{-7.08}$	7.08	7.08
25	$10^{-14.00}$	$10^{-7.00}$	7.00	7.00
30	$10^{-13.83}$	$10^{-6.92}$	6.92	6.92
40	$10^{-13.53}$	$10^{-6.76}$	6.76	6.76
50	$10^{-13.26}$	$10^{-6.63}$	6.63	6.63
100	$10^{-12.28}$	$10^{-6.14}$	6.14	6.14

Steam Explosion

Steam explosion differs from hot compressed water as at the end of pretreatment process, the pressure is suddenly released by opening the pressure valve, instead of cooling it down (Medina et al., 2016; Sun and Cheng, 2002). Steam explosion is environmental friendly as only water is needed and sudden depressurized will lead the biomass to defibrillate the bundles of cellulose, thus increase the accessibility of enzymatic hydrolysis (Stelte, 2013). Steam explosion able to break lignin structures then releasing the hemicellulose and cellulose from tight bond of lignocellulosic composition primarily introduced by Mason (1926). By steam explosion with combined severity factor, the degradation of lignocellulosic materials can enhance the hydrolysis of cellulose to produce fermentable sugar. Steam explosion usually started with temperature of 160-260°C which corresponding with pressure of 0.69-4.83 MPa for time required before pressure is released to atmospheric pressure (Bhatia et al., 2012). In previous study by Mansori (1990), hydrolysate from oil palm stem saccharification yielding 75-100% of glucose conversion, while only 8-22% of xylose conversion under condition of 10-25 kgf/cm² and 3-20 min. In recent study, Medina et al. (2016) found that OPEFB was examined to have the best pretreatment of 195°C for 6 min which resulting increasing of 24.6% of cellulose and high reduction of 68.11% hemicellulose compared to untreated OPEFB.

Superheated Steam

When sensible heat is subjected to saturated (wet) steam, it will create unsaturated (dry) steam named as superheated steam (Mahmud et al., 2013; Zakaria et al., 2015b). Superheated steam was used for more than 100 years ago in order to dry wood and coal (Kiiskinen and Edelman, 2002). On top of that, superheated steam becomes popular and the usage had been broadening into other sector such as food, paper and pulp, and many more. Besides that, it was considered as safe due to no releasing pressure in sudden condition as required in steam explosion. In addition, boilers in oil palm mill produced excess saturated and superheated steam which can be utilized towards oil palm biomass as it has been proven to glucose production (Shamsudin et al., 2012). In process of pretreatment, silica bodies are removed by superheated steam and created microtubular which will increase the surface area, thus allowing the enzymes to react efficiently with cellulose. Superheated steam pretreatment towards OPMF can produced 7.18 g/g of reducing sugar at 180°C for 60 minutes (Mahmud et al., 2013). However Zakaria et al. (2015b) reported that, in comparison of superheated steam and hot compressed water, hot compressed water provides higher recovery of cellulose content and this can be observed from alteration of OPMF morphological structure. This statement was supported by his results on removal of 94.8% hemicellulose which generating acetic acid that enhanced further decomposition of hemicellulose due to fully contact with water of hot compressed water.

Summary of biomass pretreatment methods

Regarding to three hydrothermal pretreatments had been mentioned above; each pretreatment owns advantages and disadvantages. Parameters that need to be concerned in these three pretreatment processes are time taken for a complete process, temperature involved, pressure and by-products produced after pretreatment. Hot compressed water has advantage where only water as the enhancer while steam explosion has additional of sudden pressure release after pretreatment process time completed. Superheated steam uses heated saturated steam at high temperature in the reactor. Based on these three pretreatment, hot compressed water had been identified as promising step as it did not involve any chemical, sudden release pressure and longer time. Based on three related hydrothermal pretreatments, the differences can be summarized in Table 2:

Table 2: The summary of hydrothermal pretreatment

Pretreatment	Advantages	Disadvantages or limitations	References
Hot compressed water	Self-creating of acidic condition in the bioreactor through conversion of hydronium ion from water molecules	High amount of acetic acid produced towards the end of experiment due to cleavage of acetyl bond from hemicellulose	Goh et al. (2012, 2010); Hideno et al. (2011); Kumagai et al. (2015)
Steam explosion	Reduce particle size, disrupt cell wall structure which hemicellulose degradation and lignin transformation	The disruption of lignin compound creating solubilized phenolic substance and fermentable sugar in hydrolysate	Kumar et al. (2009); Medina et al. (2016); Teng et al. (2010); Uzelac (2014)
Superheated steam	Safe and cost effective for large-scale process	Longer time taken required to complete the pretreatment	Mahmud et al. (2013); Zakaria et al. (2015b)

Conclusion

Hydrothermal pretreatment is becoming the interest of many researchers due to the ability of disruption of cell wall resulting hemicellulose to degrade and dissolution of lignin structure. Furthermore, hydrothermal is used to avoid usage of excessive chemical and being environmental friendly towards the earth. Besides that, the excessive steam from palm oil mill which often to be released to the environment, can be utilized as the precursor for the hydrothermal pretreatment. Hence, the wasting of energy can be reduced, while making something beneficial.

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