CROSSLINKING OF ALKALINE PEROXIDE OIL PALM EMPTY FRUIT BUNCH FIBRES VIA AZIDE-ALKYNE CLICK CHEMISTRY: SYNTHESIS AND CHARACTERIZATION

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by

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CHAPTER 1 – INTRODUCTION

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LIST OF SYMBOLS

AP	Alkaline peroxide
APP	Alkaline peroxide pulping
CA	Cellulose acetate
CH_3CO	Acetyl
CO_2	Carbon dioxide
CPO	Crude palm oil
Cu	Copper
DCM	Dichloromethane
DMF	Dimethylformamide
DTPA	Diethylenediaminepentaacetic
EA	Elemental analysis
EFB	Empty fruit bunch
FTIR	Fourier Transform Infrared
HCl	Hydrochloric acid
HPAC	Hydrogen peroxide-acetic acid
FTIR	Fourier Transform Infrared
g	gram
h	Hour
KBr	Potassium bromide
LM	Light microscopic
$NaNO_2$	Sodium nitrate

NaOH	Sodium hydroxide
Na_2SO_4	Magnesium sulphate
NFC	Nanofibrillated cellulose
NMR	Nuclear Magnetic Resonance
N_2	Nitrogen
N_3	Azide
OD	Oven dried
PHA	Polyhydroxylalkanoates
PTSC	*p*-toluenesulphonyl chloride
SEM	Scanning electron microscopy
SMCA	Sodium monochloro acetate
THF	Tetrahydrofuran
OH	Hydroxyl
Ppm	Parts per million
Rpm	Revolutions per minute
wt.	weight
^{o}	degree
^{o}C	Degrees Celsius
%	Percent

PENYAMBUNGSILANGAN GENTIAN-GENTIAN ALKALI PEROKSIDA TANDAN BUAH KOSONG KELAPA SAWIT MELALUI KIMIA KLIK AZIDA-ALKUNA: SINTESIS DAN PENCIRIAN

ABSTRAK

Terdapat minat yang semakin meningkat dalam pengubahsuaian gentian untuk beberapa aplikasi industri. Pengubahsuaian kebanyakannya telah dilakukan untuk meningkatkan sifat-sifat gentian. Walau bagaimanapun, maklumat mengenai pengubahsuaian gentian melalui kimia klik masih terhad. Dalam karya ini, tandan buah kosong kelapa sawit diekstrak melalui Alkaline Peroxide Pulping (APP). Kemudian, ekstrakan pulpa dipukul hingga 8000 revolusi mengunnakan PFI mill. Gentian yang terhasil akan diubahsuai secara kimia menggunakan dua strategi kimia klik dinilai untuk mengubah suai gentian tandan buah kosong kelapa sawit tanpa menggunakan tambahan pemangkin tembaga, iaitu kebolehsebaran dan penyambung-silangan. Untuk kedua-dua jenis pengubahsuaian ini, terdapat pula dua kaedah untuk mengubahsuai gentian. Penyambung-silangan telah dicirikan oleh spektroskopi Fourier Transform Inframerah, Mikroskop Pengimbasan Elektron, spektroskopi Fotoelektron Sinar-X, dan analisis unsur, manakala kebolehsebaran telah disiasat oleh Fourier Transform Inframerah, mikroskop cahaya, saiz zarah dan penganalisa potensi zeta.. Kimia klik didapati berjaya menyambung-silang dan menyebarkan gentian, berdasarkan ujian-ujian yang telah dijalankan. Penggunaan gentian terubah suai ini adalah menarik untuk penghasilan produk pembungkusan dan pulpa teracu.

CROSSLINKING OF ALKALINE PEROXIDE OIL PALM EMPTY FRUIT BUNCH FIBRES VIA AZIDE-ALKYNE CLICK CHEMISTRY: SYNTHESIS AND CHARACTERIZATION

ABSTRACT

There has been growing interest in fibre modification for several industrial applications. The modifications have mostly been done to improve the fibre properties. However, the information regarding fibre modification via click chemistry is still limited. In this work, oil palm empty fruit bunch was extracted via Alkaline Peroxide Pulping (APP). Then the extracted pulp was beaten to 8000 revolutions using PFI mill. The resulting fibres were chemically modified using two strategies of click chemistry were evaluated for modifying empty fruit bunch fibre without the addition of copper catalyst, which was dispersibility and crosslinking. In both of these modification strategies, there were two methods to modified the fibre. Crosslinking were characterized by Fourier Transform Infrared spectroscopy, Scanning Electron Microscopy, X-Ray Photoelectron Spectroscopy and Elemental Analysis, while dispersibility were characterized by Fourier Transform Infrared Spectroscopy, light microscopy, particle size and zeta potential analyzer. Click chemistry was found to successfully crosslinked and dispersed the fibers, based on the tests conducted. These modified fibres would be an interesting application for the packaging and moulded pulp products.

CHAPTER 1 INTRODUCTION

1.1 General

Cellulose is an environmentally friendly material and a polymer occurred naturally that has been drawing world attention over recent decades. It’s considered to be the most abundant and renewable natural resource on earth (Tonoli et al., 2012; Zaman et al., 2012). Cellulose is a long and linear homopolymer composed of β-D-glucopyranose units linked by (1→4)-glycosidic bonds with cellobiose as the repeating unit. It can be found in most all plants, algae, bacteria, fungi, and tunicates. The goodness of cellulose including biodegradability, low density, low cost, and good mechanical properties have contributed to many applications such a pulp and paper, textiles, composites, and pharmaceuticals (Lavoine et al., 2012; Haafiz et al., 2014).

In recent years, several studies have been made regarding chemical modification of cellulose depending on the final applications. One of the reason is due to strong hydrophilicity of this material, which limits it use in several applications such as composites. In fact, strong hydrophilicity on the surface of cellulose tends to cause agglomeration into bundles due to formation of hydrogen bonds between the hydrophilic cellulose chains. Thus, it cannot be dispersed well in most non-aqueous media and hydrophobic molecules (Benkaddour et al., 2013). For these reason, cellulose are, generally, subjected to a chemical modification in order to improve/change its properties. The presence of a large number of hydroxyl groups on cellulose make this material suitable for the introduction of new functionality. Several methods have been demonstrated to chemically modified the cellulose.

However, the most common methods used are esterification and etherification (Paquet et al., 2010; Islam et al., 2013).

New concept of “click chemistry” was introduced by Sharpless in 2001, is the reliable and most common methods to link molecules covalently, and it has been applied in wide range of applications, such as drug delivery, chemical biology and pharmaceuticals. Sharpless defined the term “click chemistry” as follows: “The reaction must be modular, wide in scope, give very high yields, generate inoffensive by-products that can be removed by non-chromatographic methods, and be stereospecific (but not necessarily enantioselective). The required process characteristics include simple reaction conditions, readily available starting materials and reagents, the use of no solvents or a solvent that is benign (such as water) or easily removed and simple product isolation” (Hein et al., 2008; Tron et al., 2008; Avti et al., 2013).

Among the various click reactions available, -thiol-ene and thiol-yne included, azide-alkyne is the most popular. Since Sharpless developed the concept of click chemistry, copper (I)-catalyzed azide-alkyne cyloaddition (CuAAC) reaction has been extensively applied in polymer science field. However, in recent years, many studies have focused in copper free click chemistry. The utilization of copper, which acting as catalyst in CuAAC reaction can be harmful due to the potential of toxicity of copper ions (Yao et al., 2013; Bordoni et al., 2015). Thiol-ene reaction is copper-free click chemistry, based on a thiol and alkene group. This reaction has several advantages, including high reaction efficiency, simple operation, metal-free catalyst and mild reaction conditions (Duo et al., 2015). Among the three most popular click chemistry, thiol-yne is less developed. This reaction known as a sister reaction to thiol-ene reaction and as complimentary process to CuAAC reaction. However, most lower molecular weight thiols are toxics (Lowe, 2014).

In this present work, azide-alkyne click chemistry has been utilized due to high selectivity, where only alkyne and azide component takes place in this reaction. In usual conditions, catalyst has been used in click reaction, which is copper-(I). However, in this work the utilization of copper-(I) has been dropped due to the toxicity risk. Previously, Yhaya and co-workers performed Huisgen's 1,3-dipolar azide-alkyne cycloaddition with a copper-(I) catalyst in drug delivery system. However, there was problem, where total copper removal was deemed impossible, even after several procedures were attempted. Other than that, it was found that copper removal process will significant product loss. Therefore, Huisgen's 1,3-dipolar azide-alkyne cycloaddition without a copper-(I) catalyst was employed. The reaction is successful and complete in 24 h at 100 ^{o}C between β-cyclodextrin azide and propargyl alcohol (Yhaya et al., 2011).

In the present work, empty fruit bunch (EFB) was extracted via Alkaline Peroxide Pulping (APP). Then the extracted pulp was beaten to 8000 revolutions using PFI mill. The resulting fibres were chemically modified to achieve i) crosslinking, and ii) dispersibility. Crosslinking in this work means joining the fibres together with covalent bonding, while dispersibility is to prevent the fibres from clumping/aggregated/agglomerate together. Furthermore, the properties of modified fibres were also analyzed and compared.

1.2 Objectives

The main objectives to be achieved in this work are:

1. To modified the alkaline peroxide empty fruit bunch fibres via azide-alkyne click chemistry.
2. To investigate the effect of chemical modification to the properties of alkaline peroxide empty fruit bunch fibres.

CHAPTER 2 LITERATURE REVIEW

2.1 Chemical Modification of Cellulose

The chemical modifications of cellulose have been widely studied over the world. Hundreds of research papers and thematic reviews related to chemical modification have been published. In the last few decades, hydroxyl groups of cellulose are subjected to chemical transformation into numerous moieties, and further imparting new properties to cellulose and make them suitable for many new applications. Several methods of chemical modifications of cellulose have been established, including acetylation, silylation, carboxymethylation, TEMPO-mediated oxidation, and as well as click chemistry (Faugeras et al., 2014).

2.1.1 Acetylation

Acetylation is where the hydroxyl groups in a chemical compounds are replaced by an acetyl group (CH_3CO-), known as cellulose acetate (CA) (Nwadiogbu et al. 2014; Zweckmair et al., 2014). In 1865, CA was first synthesized by Schuetzenberger and industrially produced in early 1900 (Cao et al., 2010). Figure 2.1 showed the reaction of CA.

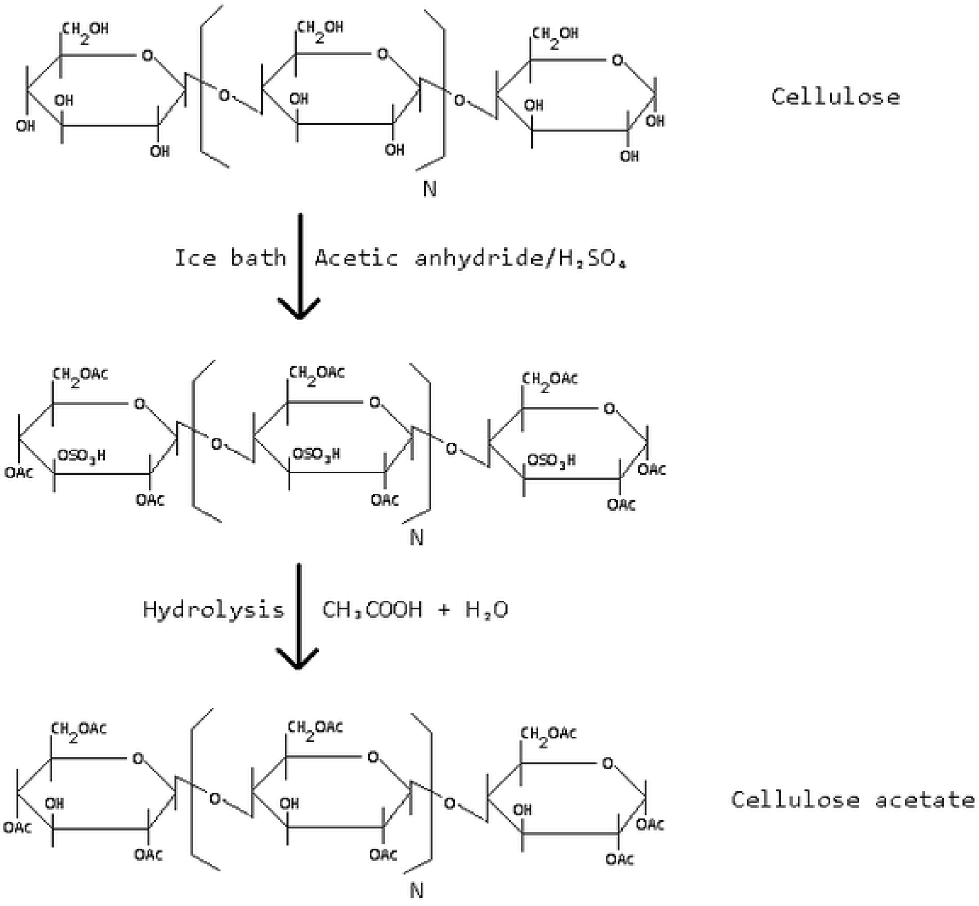

Figure 2.1 Mechanism of cellulose acetate (Anonymous, 2009).

Commercially, CA are often produced by heterogenous acetylation with an excess of acetic anhydrides as acetylating agents and in the presence of sulfuric acid or perchloric acid as catalyst (Cerqueira et al., 2007). However, this heterogenous process has limitations, which is the products are heterogenous and the direct preparation of mono and di-substitued CA is impossible owing to the different accessibilities to the –OH groups of cellulose in the crystalline and amorphous regions. Recently, scientist showed interest in a new and promising synthesis acetylation of cellulose under homogenous reaction condition, which has several advantages over the heterogenous reaction. Under homogenous reaction, the degree of substitution (DS) value can be controlled by adjusting the temperature, reaction time and molar ratio of cellulose to derivative agents, the degradation of cellulose can be avoided during reaction, reaction efficiency is higher and solvent easy to recycle (Yan et al., 2010; Huang et al., 2013).

In recent years, acetylation reaction is one of the famous techniques used for modifying the hydrophilic surface of lignocellulosic material to be more hydrophobic (Jonoobi et al., 2012; Li et al., 2016). Globally, around 1.5 billion pounds of CA produced annually and widely used in the fields of film, textile, coating, membranous filters, cigarette, cosmetic, pharmaceutical, thermoplastic and sheet for food packaging industries (Cao et al., 2007; Hindi & Abohassan 2015; El Nemr et al., 2016). Sun et al., 2004 esterified sugarcane baggase in the presence of acetic anhydride and N-bromosuccinimide as a catalyst without solvent under mild conditions for the production of oil sorption-active materials. It can be used to substitute non-biodegradable materials in oil spill cleanup.

2.1.2 Silylation

Silane is one of the techniques recognized as efficient coupling agent to modified cellulose surface and broadly used in composites (Ramamoorthy et al., 2015). As reported by Ifuku and Yano (2015), the using of γ-aminopropyltriethoxysilane (APS) as silane coupling agent on microfibrillated cellulose in composite fields showed positive effects. The fibres tend to agglomerate into bundles due to hydrogen bond formed between hydrophilic cellulose, and further unevenly distribute throughout the non polar polymer matrix. By using silane coupling agent, the dispersibility of fibres and compatibility between the fibres and matrix were improved (Ifuku & Yano, 2015). Beside, silane coupling agents extensively used in adhesive formulations (Abdelmouleh et al., 2007).

Utilization of silane coupling agent normally changed the fibres from hydrophilic to hydrophobic, improved the degree of cross-linking in the interface region, commercially available in a large scale and provides great bonding (Kalia et al., 2011; Salarizadeh et al., 2016). Basically, silane undergoes hydrolysis, condensation and bond formation stage (Xie et al., 2010). The reaction scheme is given in Figure 2.2.

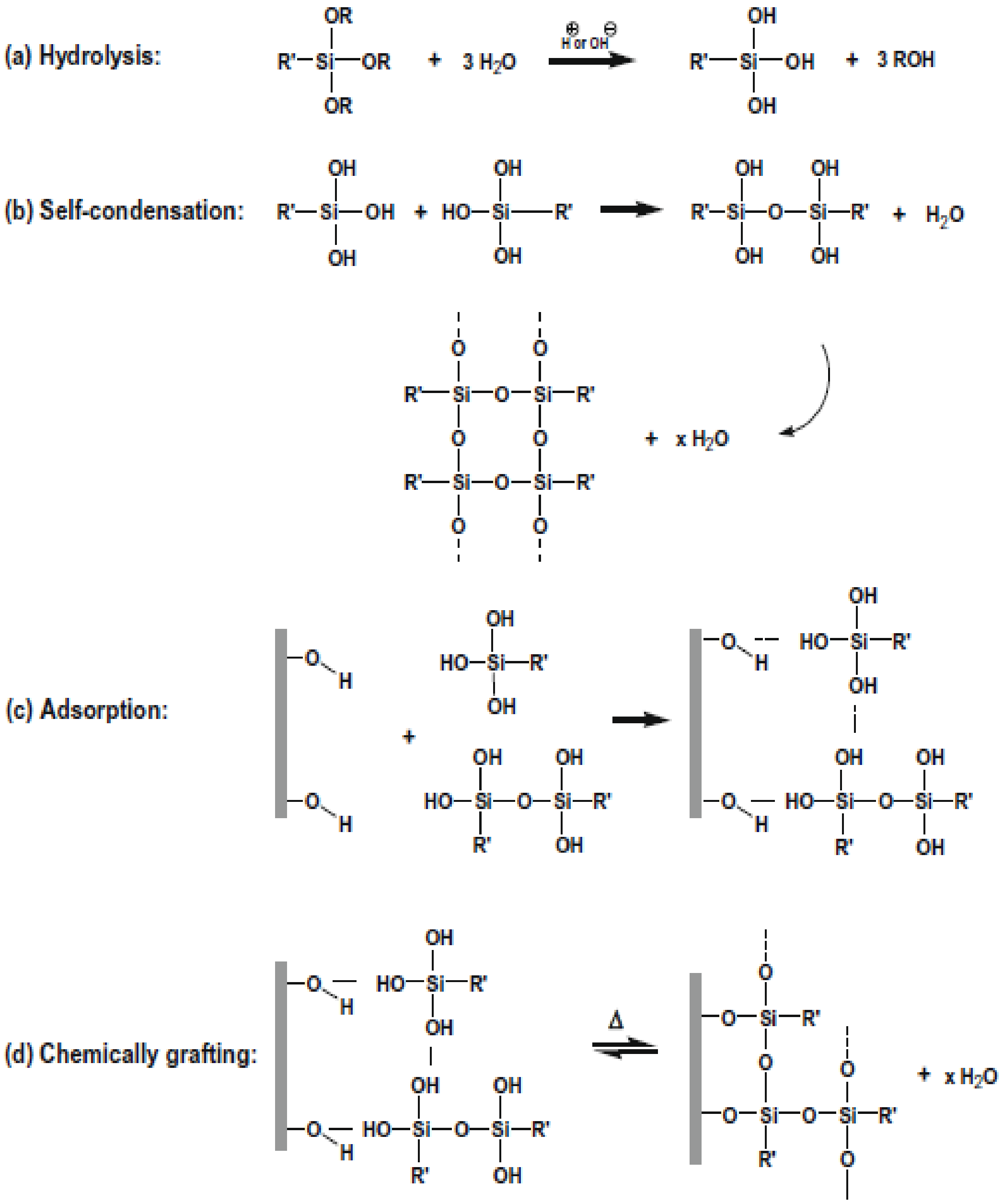

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Figure 2.2 Interaction of cellulose with silane by hydrolysis process (Xie et al., 2010).

2.1.3 Carboxymethylation

Carboxymethylation has been used to improve the utilization of cellulose and cellulose ether today is used in many applications such as in the papermaking, drug release, paint, detergent, pharmaceutical, food, and textile industries (Pushpamalar et al., 2006; Fan et al., 2014). In general, different source of various polysaccharides have been prepared by carboxymethylation such as, cellulose, xylan, chitin and scleroglucan (Yang et al., 2011). As reported by Das (2015), carboxymethyl starch had improve swelling and solubility. Moreover, morphological study showed that the degree of deformity and porous structure formed on the surface of starch granules were found to be increased (Das et al., 2015).

In this modification, introduction of carboxymethyl groups ($-CH_2COO-$) that into the cellulose enhanced its water solubility. Moreover, cellulose treated by carboxymethylation is usually less viscous, has changed its molecular weight, and has greater anionic character than the native cellulose (Bhatia & Ahuja 2015; Z. J. Wang et al., 2016).

Commercial carboxymethylcellulose (CMC) is produce on a large scale, heterogenous procedures by slurry process, and involving two steps. First, cellulose fibres are swollen in concentrated NaOH solution. In this step, the aqueous NaOH penetrates the crystalline structure of cellulose, solvates the hydroxyl groups, and further breaking the hydrogen bonds. Second, this alkali cellulose then reacted with sodium monochloro acetate (SMCA) to form carboxymethyl cellulose ethers. The production of CMC required temperature between 40 and 80 ^{o}C and take a long reaction time among 1 to 6 hour. The reactions formed by-products, including water and sodium chloride (Bhandari et al., 2012; Dos Santos et al., 2015).

2.1.4 TEMPO-mediated oxidation

Recently, 2,2,6,6-tetramethylpiperidine-1-oxy radial (TEMPO)-mediated oxidation becomes very common chemical modification, as it is created opportunities to introduce carboxylic groups, via the intermediate aldehyde stage at the C-6 of native and man-made cellulose fibres or bacterial cellulose (Fitz-Binder & Bechtold, 2014). The most studied TEMPO-oxidation process is based on the use of TEMPO/NaOCl/NaBr system and often performed at pH 10 or higher. During the oxidation, the amount of bromide is commonly higher than the amount of TEMPO (mass ratio 10:1) (Pääkkönen et al., 2015). The mechanism of TEMPO-mediated oxidation of cellulose is summarized in Figure 2.3.

TEMPO-mediated oxygen represents several advantages, such as very selective and effective conversion of alcoholic hydroxyls to carboxyls under aqueous conditions, the reaction rate and the yield are high, the process is catalytic and inexpensive (Milanovic et al., 2013). Additionally, this modification is water-soluble and nitroxyl or nitroxide radicals involved are extremely stable (Hirota et al., 2009).

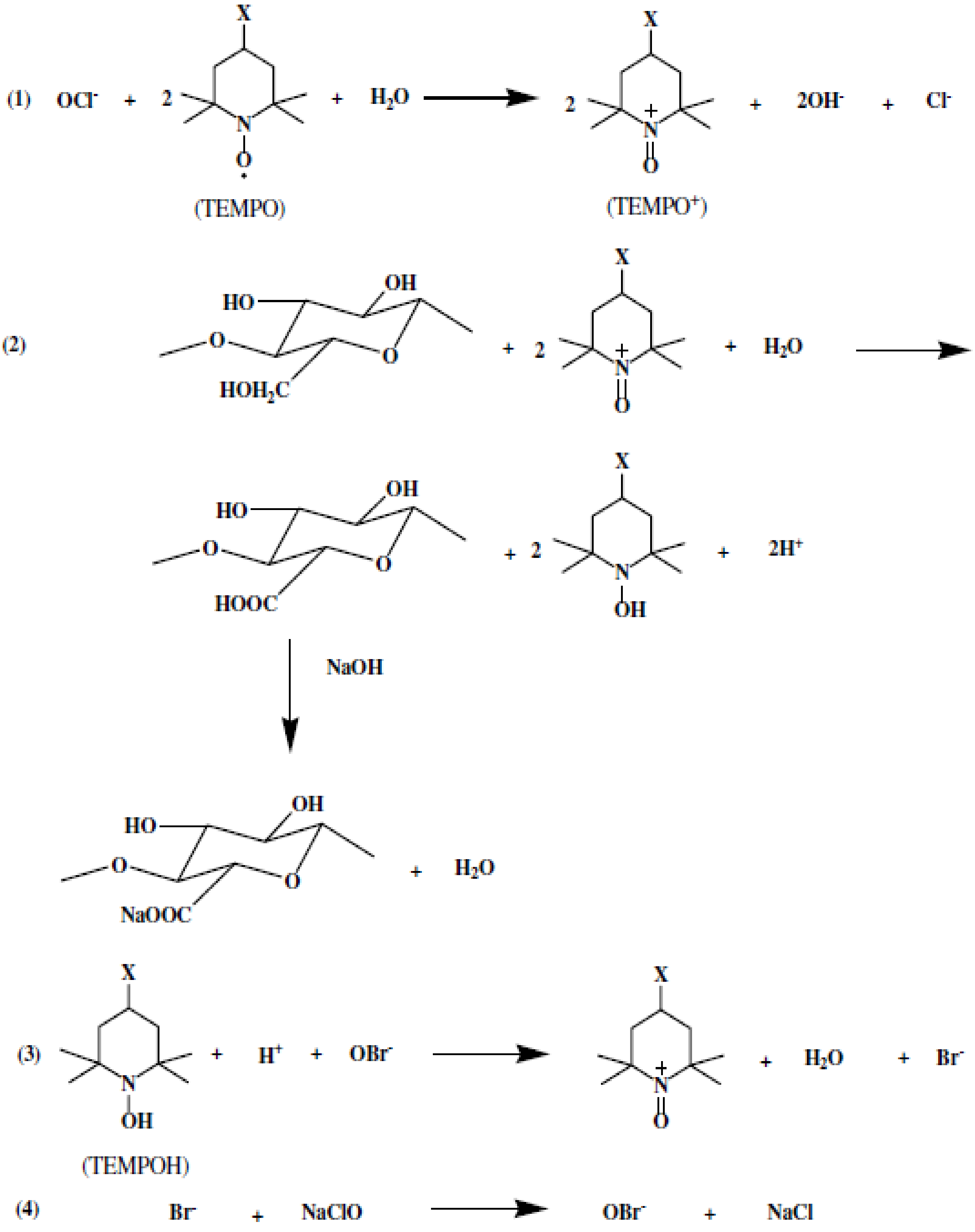


Figure 2.3 Mechanism of TEMPO-mediated system of cellulose (Dang et al., 2007).

2.1.5 Click Chemistry

Click chemistry is recognized as a powerful chemical reaction with great bioorthogonality features, including rapid, highly specific, and biocompatible in biological environments (Zhang & Zhang, 2013). Click chemistry has gained attention in the modification of cellulose and several articles on the topics can be found in the literature (Sadeghifar et al., 2011; Karaaslan et al., 2013; Yadav et al., 2015).

Copper (I)-catalyzed azide-alkyne cycloaddition (CuAAC) is one of the most used click reaction employed to cellulose. As reported by Pahimanolis (2011), the surface functionalization of nanofibrillated cellulose (NFC) was performed by CuAAC reaction are successful without solvent exchange or drying steps involved in the synthesis. Azide functional groups were introduced onto NFC backbones, and then reacted with propargyl amine in the present of copper as catalyst. The reaction was able to link two moieties together in a very reliable and efficient way (Pahimanolis et al., 2011). In this present work, click chemistry was employed to modify empty fruit bunch fibres to improved fibre properties.

2.2 Click Chemistry Reaction

The term of "click chemistry" first coined by Sharpless and co-workers in 2001, nowadays has gained great attention across nearly all areas of modern chemistry. The impressive term "click" refers to efficient, versatile chemical transformations and selective reaction leading to a single reaction product (Lutz & Zarafshani, 2008).

Up to now, click chemistry is broadly used in several applications, such as drug discovery, pharmaceutical and polymer. Based on Figure 2.4, the graph showed percent of total publications included journal articles, patent, reviews, abstract, preprints, and dissertations in four research areas. The “other” category refers to research area in material sciences, certain reviews, and novel methods for improved catalyst (Hein et al., 2009).

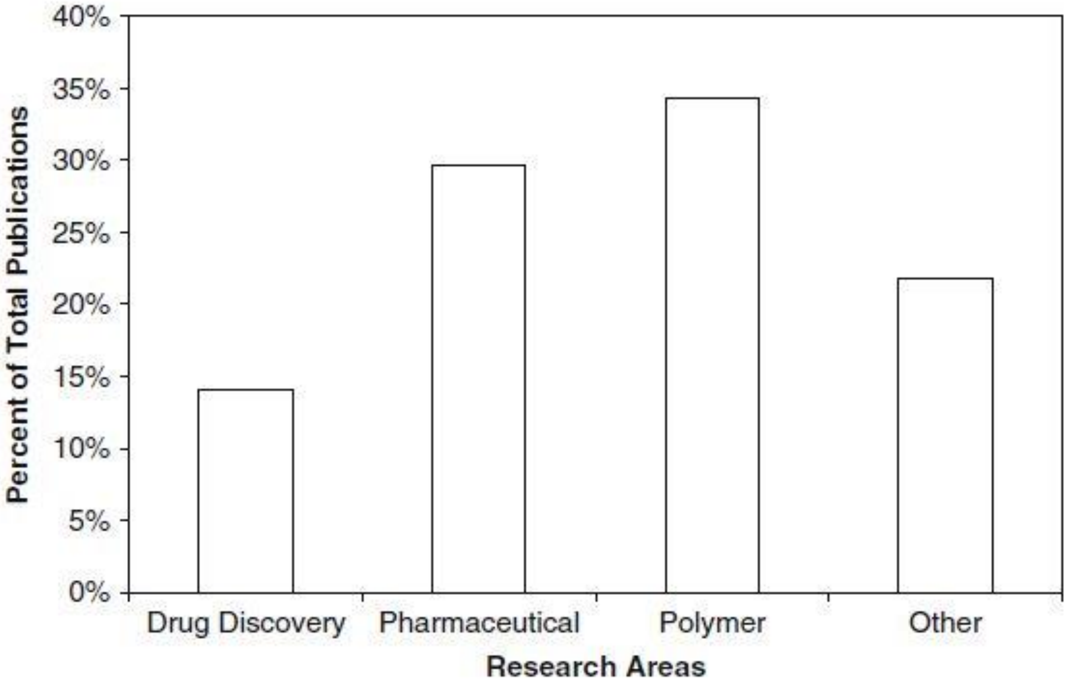


Figure 2.4 Percent of total publication in four research areas (Hein et al. 2009).

To date, several reactions fall into the concept of click chemistry, including Copper(I)-Catalyzed Alkyne-Azide Cycloaddition (CuAAC), thiol-based reactions such as thiol-ene, Diels-Alder reaction and the Strain promoted azide-alkyne cycloaddition (Figure 2.5) (Ramdas et al., 2016; Meng & Edgar, 2016). Among them, CuAAC reaction is the most popular and one of the most powerful tools in medicinal chemistry (Aragao-Leoneti et al., 2010).

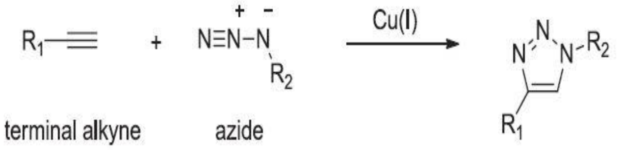
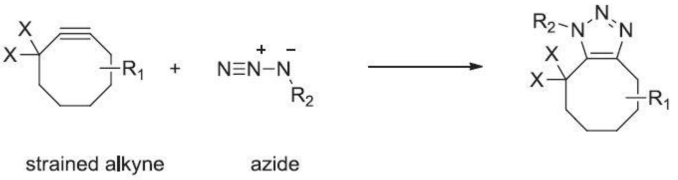
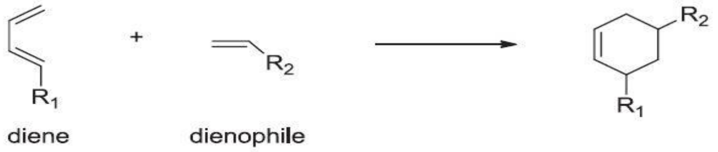
Copper(I) Azide-Alkyne Cycloaddition (CuAAC)	
Strain-Promoted Azide-Alkyne Cycloaddition (SPAAC)	
Diels-Alder	
Thiol-ene	

Figure 2.5 Click reactions that are commonly used in polymer chemistry (Lava et al., 2015).

2.2.1 Copper (I)-Catalyzed Azide-Alkyne Cycloaddition

Copper (I)-catalyzed azide-alkyne cycloaddition (CuAAC) reaction is a Huisgen 1,3-dipolar cycloaddition of azide with terminal alkynes to formed 1,4-disubstituted 1,2,30-triazoles in the presence of copper. In fact, the 1,3-dipolar cycloaddition of azides with terminal alkynes at first discovered by Huisgen in 1963. It was largely ignored for decades due to the original Huisgen reaction did not show regioselective and required high pressure and temperature. Early 2002, in simultaneous and independent studies, research groups of Sharpless and Meldal reported that the utilization of catalyst by Cu(I) complexes in the click reaction greatly enhanced the reactivity the click reaction up to 10^7 rate enhancements (Pasini, 2013; Li et al., 2013; Avti et al., 2013).

The CuAAC reaction fulfills all of the criteria of click chemistry perfectly. CuAAC can be performed over a wide range of temperatures, starting from 0 ^oC to 160 ^oC, are compatible with water and water-miscible solvents, such as dimethylformamide (DMF) and tetrahydrofuran (THF), and can tolerate with oxygen. The reaction between azides and terminal alkynes are easily to install, extremely stable, purification essentially consist of product filtration, and unaffected by steric factors (Hein et al., 2009; X. Wang et al., 2016).

The CuAAC reaction has been successfully introduced and developed in contemporary life sciences, such as biomedicine, material science, chemical biology, cell biology and nano-technology (Ladomenou et al., 2016; He et al., 2016). Recently, the CuAAC reaction was carried out by the addition of azide and alkyne to form a triazole ring connecting two cellulose chains shown in Figure 2.6. CuAAC reaction employed as chemical functionalization onto cellulose in order to improve the dry or wet strength of the paper. The reaction has ability to create three-dimensional network without using traditional crosslinking reagents. From the result obtained, the physical properties of sheets containing modified fibres showed that chemical functionalization had occurred between fibres and that it had a positive effect on the elongation of the sheets. Thus, the modification of fibres by the CuAAC reaction was successful and can be used in several applications, such as moulded pulp products and packaging (Faugeras et al., 2014).

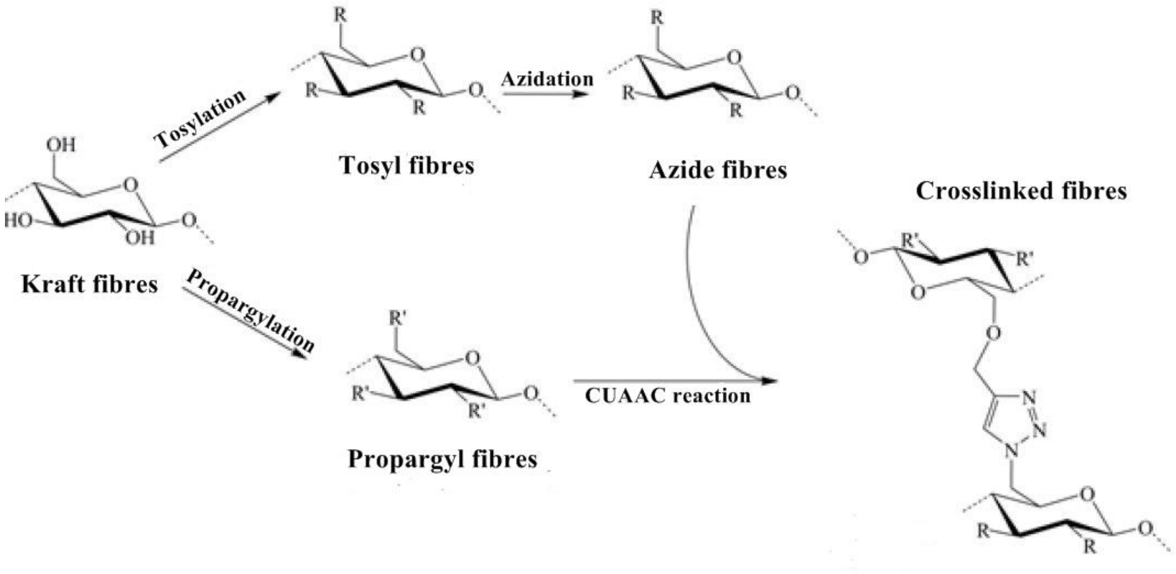
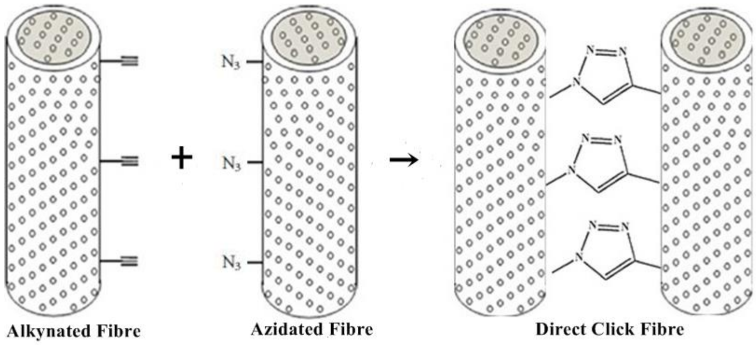
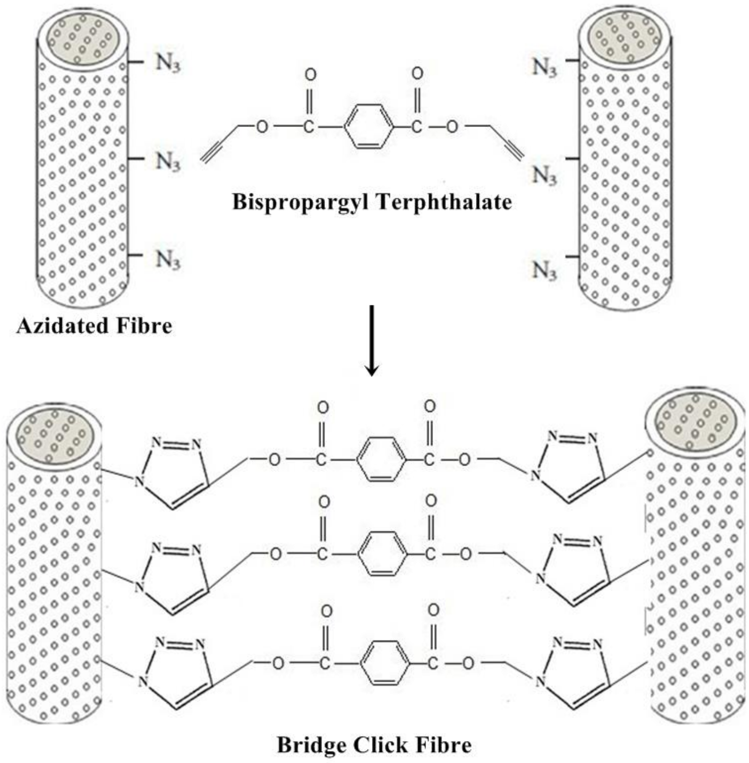


Figure 2.6 Modification of fibres by CuAAC reaction (Faugeras et al., 2014).

However, there are limitations of CuAAC chemistry which need to be taken into account. The toxicity of Cu(I), which is capable of mediating the generation of reactive oxygen species (ROS) from O_2, and further causes damage to living cells need to be considered. Recently, Cu-free click strategies have been developed to solved the problems. In this study, Huisgen 1,3-dipolar cycloaddition of azide with terminal alkynes without Cu(I) had been employed to modify oil palm empty fruit bunch (OPEFB) fibres, and further improved the properties of fibres. Figure 2.7 and 2.8 showed the illustration two strategies of fibres modifications using azide-alkyne click chemistry reaction.

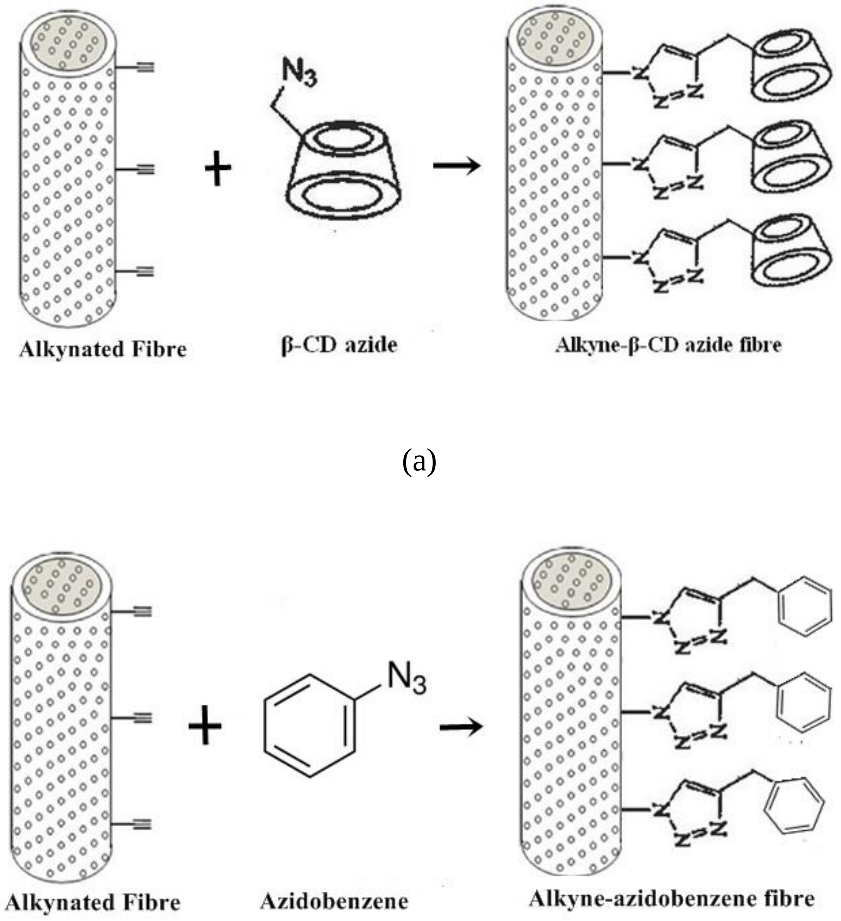


(a)



(b)

Figure 2.7 Illustration of fibre modification to achieve crosslinking (a) Direct click fibre and (b) Bridge click fibre.



(a)

(b)

Figure 2.8 Illustration of fibre modification to achieve dispersibility (a) Alkyne-β-CD azide fibre and (b) Alkyne-azidobenzene fibre.

2.3 Oil Palm

Oil palm (Elaeis guineensis) (Figure 2.9) is an ancient tropical tree crop originated from West Africa, but now planted all over the world. The native habitat of oil palm is tropical rainforest and to grow well, it requires fair amount of sunshine, hot climate, wet and humid tropic conditions. Oil palm grows on wide a range of soil, as long as it is well watered. Indonesia has been recognized as a largest palm oil producer in the world, followed by Malaysia, with production area 8,150,000 ha and 4,620,000 ha, respectively. Other oil palm producers are Thailand (720,000), followed by Nigeria (440,000 ha), Columbia (354,000 ha), and other countries (2,188,000 ha) (Awalludin et al., 2015; Oosterveer, 2015; Mba et al., 2015).

Figure 2.9 Oil palm trees in palm plantation (Anonymous, 2015).

Oil palm is now the most consumed vegetable oil in the world, with a production of 59.23 million tons in 2014 (Garcia-Nunez et al., 2015). This oil has a unique profile, where it is the only vegetable oil with almost 50-50 composition of saturated and unsaturated acid. Other than that, the oil has beneficial effect on cholesterol level and enriched with antioxidants, which make it suitable for various food applications. Oil can be extracted from crude palm oil (CPO) from the outer mesocarp and palm kernel oil (PKO) from the endosperm (Lim et al., 2015; Mba et al., 2015). CPO is mostly used in foods, while PKO is used in various non-edible products, such as cosmetics, detergents, surfactants, plastic, herbicides, and agricultural chemical (Sheil et al., 2009).

Apart from CPO and PKO, oil palm generates a substantial amount of residual biomass including empty fruit bunch (EFB), palm kernel shell (PKS), oil palm trunk (OPT) and oil palm fronds (OPF). They are generated during oil palm processing, oil palm replantation or after the oil palm fruit harvesting. These residual biomasses create the opportunity to develop value-added products. Past studies reported that the residual biomass could be potentially utilized as source of energy, pulp and paper, animal feed, medicines, and food ingredients. Through thermochemical conversion, some of residual biomass is converted into gasification, direct combustion, pyrolysis, and liquefaction (Santosa, 2008; Awalludin et al., 2015).

2.3.1 Empty Fruit Bunch (EFB)

Empty Fruit Bunch (EFB), as shown in Figure 2.10 is the major biomass that can be obtained abundantly after fruit removal for the production of CPO. In the past, EFB was burnt for energy production or even burnt in the plantation without any profit (Dermawan et al., 2013). Nowadays, the biomass used commercially as raw materials for pulp and paper, composites, medium-density fibreboard, mats, mattresses, light furniture, cushions and steam generation by burning (Alam et al., 2011; Ghazali et al., 2013).

Figure 2.10 Oil palm empty fruit bunch (Anonymous, 2012).

Other than that, an several amount of research has been done to convert EFB biomass to biofuels, such as butanol, ethanol, bio-oil, hydrogen, and biogas (Geng, 2013). In recent study, Ibrahim and co-workers (2015) converted EFB biomass into butanol using single process. EFB served as fermentation feed-stock due to its chemical compositions. It was composed of high percentage of cellulose and hemicellulose, which can be converted into sugar monomers (hexoses and pentoses sugar). Generally, the conversion of EFB biomass to butanol involve several steps, including pretreatment, saccharification, sugar recovery, ABE (Acetone-Butanol-Ethanol) fermentation, and the last step was product recovery. Pre-treatment was an important step to enhance the digestibility of the materials. In this step, lignin was removed, so the internal part of cellulose and hemicelluloses can be accessed. The next step was saccharification process, where the purpose of this process was to hydrolyze the cellulose and hemicelluloses using either acid or enzyme. Sugar recovery was a separation process of the remaining solid EFB biomass left after saccharification process. After that, the sugar can be used as carbon source for ABE fermentation. Overall, all of the processes contributed to the high cost for materials and apparatus and took much longer time. Therefore, Ibrahim and co-workers implemented the saccharification process, sugar recovery and ABE fermentation into a single process (simultaneous process), performed at the same time, and in the same vessel. The study was successful, in which the ABE yield and hydrogen production was higher as compared to two-step process (general process) (Ibrahim et al., 2015).

Due to its chemical composition, EFB biomass can be used in pulp and paper industry. The pulp and paper industry preferred the use of non-wood of plant species such as bamboo, straw, cereal, sugarcane, flax, hemp, jute as compared to wood of plant species. In addition, the utilization of non-wood can reduce the burden on forest (Singh et al., 2013). As reported by Dermawan (2013), EFB biomass was converted to pulp via the concept of alkaline peroxide pulping process. This pulping was better than chemical pulping, such as kraft and soda. The features included high pulp yield in the range 70-80 %, high brightness of 60 % to 74 % without bleaching, low