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EFFECT OF PRE-TREATMENT ON THE BLEACHABILITY OF TROPICAL MIXED HARDWOOD KRAFT PULPS TOWARDS OXYGEN AND MODIFIED OXYGEN DELIGNIFICATION

by

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LIST OF ABBREVIATIONS AND SYMBOLS

•O-O•	Singlet oxygen
A_C	Alkali charge
A_{hot}	Hot acid stage
AOX	Adsorbable oxygen halides
AP	Acidic peroxide
AQ	Anthraquinone
BL	Blue light
BOD	Biological oxygen demand
C=O	Carbonyl group
Ca	Caro's acid
CED	Cupriethylenediamine
CEH-Stage	Chlorination and alkaline extraction then ended with a hypochlorite stage
CE-stage	Chlorination and alkaline extraction
$CH_3CO_3^-$	Peracetate ion
CH_3CO_3H	Peracetic acid
Cl	Chlorine
C-O	Carbon-Oxygen bond
Co	Cobalt
COD	Chemical oxygen demand

cP.	Centipoise
C-stage	Chlorination stage
Cu	Copper
Cu^{2+}	Cupric ion
DABCO	Diazabicyclooctane
DP	Degree polymerization
DPa	Distilled peracetic acid
DTPMPA	Diethylenetriamine-penta-methylene phosphonic acid
ECF	Elemental chlorine free
EFB	Empty fruit bunch
ESR	Electron spin resonance
Fe	Iron
Fe^{2+}	Ferrous ion
Fe^{3+}	Ferric ion
FID	Flame ionization detector
FTIR	Fourier transfer Infra Red
G unit	Guaiacyl units
GC	Gas chromatography
H^{+}	Hydrogen ion
H_2O	Water
H_2O_2	Hydrogen peroxide

H_2SO_4	Sulphuric acid
HexA	Hexenuronic acid
HO^-	Hydroxyl anion
HO•	Hydroxyl radical
HOO^-	Hydroperoxide anion
HOO•	Hydroperoxy radical
KBr	Potassium bromide
KI	Potassium iodide
KIO_3	Potassium iodate
$KMnO_4$	Potassium permanganate
K_n	Kappa number reduction
M^+	Metal ion
MeGlcA	4-O-methyl-D-glucuronic acid
$MgSO_4$	Magnesium sulphate
Mn	Manganese
Mn^{2+}	Manganese ion
$Na_2S_2O_3$	Sodium thiosulphate
$Na_4P_2O_7$	Tetrasodium pyrophosphate
NaOH	Sodium hydroxide
O_2	Oxygen gas
$O_2•^-$	Superoxide anion radical

OH^-	Hydroxide ion
OH	Hydroxyl group
OH^+	Hydroxonium ions
OpAQ	Anthraquinone aided hydrogen peroxide reinforcement oxygen delignification
Op-stage	Hydrogen peroxide reinforcement oxygen delignification
O-stage	Oxygen delignification
PCDDs	Dibenzo-p-dioxin
PCDFs	Dibenzofuran
Peracetic acid	PAA
P_o-stage	Pressurized hydrogen peroxide reinforced oxygen delignification
P-stage	Hydrogen peroxide delignification stage
Px	Peroxymonosulphuric acid
Pxa	Mixed peroxymonosulphuric acid
RB	Rose Bengal
S unit	Syringyl units
SEM	Scanning electron microscopy
SFI	Sabah Forest Industries
TCF	Totally chlorine-free
UL	Long wavelength (369nm) ultraviolet light
US	Short wavelength (254nm) ultraviolet light

UV	Ultraviolet
Z-stage	Ozone stage

KESAN PRA-RAWATAN KE ATAS KEBOLEHLUNTURAN PULPA KRAFT KAYU KERAS CAMPURAN TROPIKA TERHADAP DELIGNIFIKASI OKSIGEN DAN DELIGNIFIKASI OKSIGEN TERUBAH

ABSTRAK

Delignifikasi oksigen (peringkat-O) adalah pringkat yang paling penting (selaku peringkat pertama) dalam turutan pelunturan bebas-klorin untuk penyingkiran lignin secara pukal, jadi, pemaksimuman kepilihan serta kecerahan pulpa pada peringkat-O adalah mustahak. Kecekapan peringkat-O biasa terhadap pulpa kraft campuran kayu tropika adalah dihadkan pada 38% penurunan nombor kappa dan 0.53 kepilihan. Dalam kajian ini, kecekapan peringkat-O telah dipertingkatkan melalui tiga pendekatan modifikasi iaitu, penguatan dengan aditif, pra-rawatan foto and kombinasi dua pendekatan modifikasi. Keberkesanan ketiga-tiga pendekatan modifikasi diuji berdasarkan sifat-sifat pulpa iaitu kappa nombor, kelikatan pulpa, kepilihan, kandungan asid hexenuronic dan kecerahan pulpa. Keputusan yang diperoleh menunjukkan ketiga-tiga pendekatan modifikasi berupaya meningkatkan kepilihan pelunturan sama ada dengan mempertahankan kelikatan pulpa yang tinggi atau pencapaian penurunan nombor kappa yang lebih tinggi. Bagi modifikasi penguatan dengan aditif, peringkat-O yang diperkuat dengan hidrogen peroksida (peringkat-Op) telah meningkatkan kepilihan ke 0.71 dengan meningkatkan penurunan kappa nombor sementara peringkat-Op dengan bantuan AQ dapat meningkatkan kepilihan ke 0.83 dengan mempertahankan kelikatan pulpa. Kajian terhadap pra-rawatan foto dengan dan tanpa PAA adalah satu pendekatan baru dengan tujuan untuk meningkatkan keberkesanan delignifikasi oksigen pada pulpa

kraft kayu tropika. Berdasarkan analisis spektrofotoskopi fourier transform infra merah terhadap pulpa dan lignin yang diekstrakkan, peningkatan tahap delignifikasi kemungkinan besar adalah disebabkan oleh perubahan struktur di dalam sisa lignin, manakala pra rawatan foto berupaya mengekalkan kelikatan pulpa yang tinggi adalah mungkin disebabkan oleh pengurangan kandungan kumpulan karbonil di dalam pulpa. Selain itu, pra rawatan foto juga memberi kesan yang lebih baik terhadap penyingkiran asid hexenuronic sehingga 65%. Walau bagaimanapun, kombinasi dua pendekatan modifikasi dengan pra-rawatan foto-PAA tidak menunjukkan peningkatan kepilihan pelunturan yang lebih lanjut sedangkan pulpa tersebut telah mencapai tahap delignifikasi dan kecerahan pulpa yang maksimum. Selain itu, pengekalkan kelikatan pulpa yang tinggi sama ada dengan penguatan dengan aditif dan pra-rawatan telah mempertingkatkan sifat-sifat kekuatan mekanik kertas yang dihasilkan secara ketara. Keputusan kajian yang diperoleh menunjukkan bahawa penguatan dengan aditif dan pra rawatan telah memaparkan kesan-kesan yang bermanfaat terhadap peringkat-O dengan mempertingkatkan kepilihan, kecerahan dan sifat-sifat kertas.

EFFECT OF PRE-TREATMENT ON THE BLEACHABILITY OF TROPICAL MIXED HARDWOOD KRAFT PULPS TOWARDS OXYGEN AND MODIFIED OXYGEN DELIGNIFICATION

ABSTRACT

Oxygen delignification (O-stage) is the most important stage (as first stage) in chlorine-free bleaching sequence to remove lignin in bulk, thus, maximizing of O-stage bleaching selectivity as well as pulp brightness is essential. The efficiency of the ordinary O-stage towards the tropical mixed hardwood kraft pulp was limited to about 38% kappa number reduction and selectivity of 0.53. In this study, the efficiency of O-stage was improved through three different modification approaches namely, additive reinforcement, photo pre-treatment and the combination of the two modification. The effectiveness of the three modification approaches were evaluated based on pulp properties namely kappa number, pulp viscosity, selectivity, hexenuronic acid content and pulp brightness. The results obtained showed that the three modification approaches were capable of improving the bleaching selectivity either by retaining higher pulp viscosity or attaining higher kappa number reduction. For additive modification, the hydrogen peroxide-reinforced O-stage (Op-stage) improved the selectivity to 0.71 by increasing the kappa number reduction while anthraquinone aided Op-stage increased the selectivity to 0.83 by retaining the pulp viscosity. Thus, the selectivity of the Op-stage and OpAQ was improved from 0.53 to 0.71 and 0.83, respectively. The studies of the photo pre-treatment with and without PAA were a new approach with the aim to improve the effectiveness of O-stage on tropical hardwood kraft pulp. Based on the analysis of fourier transform infrared spectroscopy of pulp and extracted lignin, the increased degree of

delignification might mainly due to the structural changes of the residual lignin, while photo pre-treatment could retain higher pulp viscosity probably due to the content of carbonyl group in pulp was diminished. Moreover, photo pre-treatment also give better effect on elimination of hexenuronic acid up to 65%. However, the combined modification approach with the pre-treatment of photo-PAA did not further increase the bleaching selectivity and pulp brightness as the pulp had achieved its maximum extent of delignification by photo pre-treatment alone. On the other hand, the retained higher pulp viscosity by either pre-treatment or additives reinforcement was significantly improved the mechanical properties of the paper. The results obtained showed that pre-treatment and additives reinforcement exhibited beneficial effects to the O-stage by enhancing the selectivity, brightness and paper properties.

CHAPTER 1 INTRODUCTION

1.1 General

Conventionally, pulp bleaching is performed with an aid of chlorine gas as the first bleaching stage followed by alkaline extraction to achieve high degree delignification. Chlorination is the most efficient bleaching agent and least expensive among all the bleaching chemicals (Tench and Harper 1987, Barroca et al. 2001, Suchy and Agryropoulos 2002). However, bleaching by using the elemental chlorine creates by-products such as polychlorinated dibenzo-p-dioxins, chlorinated pesticides, polychlorinated biphenyls, chlorofluorocarbons and polychlorinated dibenzofurans which are harmful to the environment and they are highly related to ill-health. Environmental concerns relating to the generation of polychlorinated organic materials have led to a rise in demand on the chlorine-free delignified pulp and paper products. Besides the pressure from the environmentalist organizations and also pulp and paper consumers, the implementation of stringent environmental regulation by the government also forces the pulp and paper industry to minimise the consumption of chlorine in the pulp and paper production (Parthasarathy et al. 1990, Leroy et al. 2004, Ng et al. 2011).

As the first move in the pulp bleaching revolution, oxygen delignification (O-stage) is used in conjunction with chlorine and chlorine dioxide in the delignification process with the aim to reduce the consumption of chlorine-based chemicals (Ismail and Guniz 2008, Leh et al. 2008). However, to completely eliminate the use of chlorine-based chemical in bleaching plant, totally chlorine-free (TCF) bleaching should be adopted. TCF is fairly widely used to describe pulp bleached without any chlorine-based compounds from bleaching and the effluent discharged has less toxicity in comparison to conventional bleaching (Agarwal et al. 1999, Sippola and Krause 2005).

The O-stage is a conventional pre-bleaching stage and is capable of removing residual lignin up to 50% in the unbleached pulp before entering the bleaching plant as it is relatively more economic and energy saving (Rwaichi 1998, Gaspar et al. 2003). Principally, molecular oxygen is a non-hazardous, renewable, low-cost and widely available reagent. Hence, molecular oxygen is best option for replacing the undesirable chlorine-based chemicals (McDonough 1996). However, the delignification of the O-stage is traditionally limited to no more than 50% and beyond the limit, the resultant pulps show lower strength properties due to low selectivity between delignification and carbohydrates degradation (Vishal 2001, Ng et al. 2011).

For attaining a more efficient TCF bleaching, many researchers had been carried out by adding the additives such as bis(o-phenanthroline)copper, diethylenetriamine-penta-methylene phosphonic acid, hydrogen peroxide (H_2O_2), 1,10-phenanthroline and etc. to improve the oxygen delignification (Parthasarathy et al. 1990, Johansson and Ljunggren1993, Stevens and Hsieh1995, Lachenal1996, Potůček and Milichovský 2000, Sippola and Krause2005, Hedjazi et al. 2009). The modified O-stage even though shows better improvement on delignification efficiency than the ordinary O-stage, its beneficial effect is limited as it lowers the pulp viscosity during the modification or increase the load of the sewage treatment process. Thus, the modification of O-stage as mentioned earlier still consists some drawbacks and consequently, which is not an ideal TCF bleaching method to be implemented in the pulp mills (Lachenal et al. 1986, Klein et al. 1990, Dence and Reeve 1996, Suchy and Argyropoulus 2002).

In 2010, Ng and co-worker recommended a higher H_2O_2 charge (> 0.5%) and small amount of anthraquinone (AQ) (0.02%) added in the O-stage on oil palm empty fruit bunch (EFB) soda-AQ pulp. The results of studies have proven that the addition of H_2O_2

and AQ during O-stage generally gives a satisfactory acceleration on the pulp brightness and minimizing cellulose deterioration while retain a higher degree of delignification in comparison to ordinary stage, thus, improve bleaching selectivity (Farley 1973, Parthasarathy et al. 1990, Ng et al. 2011). Nevertheless, there is no further modified O-stage's research had been done or continued on different chemical pulps even though the capability of the OpAQ bleaching process is remarkable.

On the other hand, many researches have been carried out by implementing a pre-treatment prior the O-stage in order to improve bleaching selectivity with the aim to enhance the degree of delignification. According to Fossum and Marklund (1988), acidic pre-treatments (such as hydrogen peroxide, sulphur dioxide, nitrogen dioxide, chlorine and others pre-treatment) tend to have a larger positive effect on the selectivity in the subsequent O-stage as compared to alkaline pre-treatments It is stated that the employments of the pre-treatment can reduce the consumption of delignifying chemical and hence, lesser the possibility of unwanted side effects to occur during the delignification process (Suss and Helming 1987, Fossum and Marklund 1988, Liebergott 1994, Stevens and Hsieh 1995, Ng et al. 2011, Chong et al. 2013).

A number of studies have proven that treatment with peracetic acid (PAA) will ease the delignification by exercising a "stimulating" effect on the bleaching process (Fossum and Marklund 1988, Roncero el at. 2002, Koay and Leh 2007). Studies have verified that lignin macromolecules are reactive under acidic conditions with presence of peracetic acid, probably through reactions involving free radicals. The reactive species of PAA is hydroxonium (OH^+) ions, which is reactive to both phenolic and non-phenolic types of lignin (Fossum and Marklund 1988, Liebergott 1994, Abad et al. 2002, Kishimoto et al. 2003). As only the phenolic type of lignin is degraded during the O-

stage, the employment of PAA pre-treatment, which is capable of degrading non-phenolic lignin, may enhance lignin degradation reactivity during succeeding stages (Obst et al. 1979, Liebergott 1994, Minja et al. 1997, Abad et al. 2002). This indicated that an application of a pre-treatment has high potential to enhance the effect of oxygen delignification and increase its selectivity.

A number of researches also reported that when lignocellulosic materials are exposed to radiation, they will generate active species (especially radicals), and thus, cause radical-induced depolymerisation of lignocellulosic materials into lower molecular weight materials (Kringstad 1969, Hon 1983, Schmidt et al. 1991, Davidson 1996, Bikova and Treimanis 2004). Thus, lignin is degraded into a lower molecular weight by radical-induced depolymerisation (Bikova and Treimanis 2004, Chong et al. 2013). Lignin shows a higher absorbency of the radiation than carbohydrates, even at different wavelengths, as it contains various chromophoric structures. Some studies report that lignin is capable of absorbing wavelengths in the range of 280 to 400 nm (Bikova and Treimanis 2004, George et al. 2005, Pandey and Vuorinen 2008). Some researchers also found that photo irradiation may affect the optical properties of lignocellulosic materials such as photo-bleaching on the pulp, especially unbleached high-yield pulp (Sun et al. 1996, Bikova and Treimanis 2004, Chong et al. 2013).

Based on this finding, irradiation degradation is possible to be applied as one of pre-treatment to cleavage or induced the structural changes in the lignin in order to increase the delignification efficiency in the subsequent bleaching stage (Fossum and Marklund 1988, Sun et al. 1996, Ng et al. 2011, Chong et al 2013). According to Sun et al. (1996) and Chong et al.(2013), the addition of peroxide-aided photo treatment in a TCF bleaching sequence can successfully increase bleaching selectivity and hence, it

shows the potential in improving O-stage selectivity. Besides that, according to William (2005), under a photo treatment, acid-treated specimen shows 1.5 times more lignin and cellulose degradation than specimens treated with water (Sun et al. 1996, Andrady et al. 1998, William 2005, Chong et al.2013). However, the reason to increase the bleaching selectivity by the photo pre-treatment has not been clearly discussed.

Generally, wood is the major raw material contributes for world pulp raw materials which accounts to ca. 90% of the world paper production. However, the forest area is decreasing and it is hard to supply the pulpwood continuously from the forests for the pulp and paper industry over the next three years (Hall 2015, Jesse 2015, CEPI 2015). To overcome this issue, plantation of fast growing species must be established to compensate the declining supply from natural forests (Cossalter and Smith 2003, FAO 2005, Jahan 2007). Fast wood plantation can produce 1.5-2 times more wood per hectare per year, and reach maturity 2-3 times faster than longer-rotation wood plantations (Cossalter and Smith, 2003).

Since 1980s, the main tropical fast growing short-rotation hardwood species planted in the most countries of South-east Asia (namely Brunei, Myanmar, Vietnam, Laos, Thailand, Malaysia, Indonesia and etc) are *Acacia mangium*, *Tectona grandis*, *Khaya ivorensis*, *Hevea brasiliensis*, *Paraserianthes falcataria*, *Gmelina arborea* and *Eucalyptus deglupta* (Lee 2003). These trees would be planted in large-sized plantations so that the amount of pulp production is sufficient within 6-8 years in one site (FAO 2002, Jusoh et al. 2014, Hashim et al. 2015). Hence, it is necessary to examine the bleachability of hardwood pulp by using the TCF bleaching processes.

1.2 Problem statement and justification

From the point of view of environmental sustainability, chlorine-free bleaching process is more environmental compatible compared to the conventional chlorine based bleaching process. Since 1980s, more environmentally friendly bleaching process namely elementary chlorine-free (ECF) and totally chlorine-free (TCF) bleaching are developed with the aim to lessen the amount of toxic chlorinated compounds released into downstream effluents (Dence and Reeve 1996, Leroy et al. 2004, Leh et al. 2008, Ng et al. 2011). Moreover, since O-stage is capable of removing the residual lignin in the pulp up to 50% without significant detrimental effect on the pulp strength, it is commonly applied as first bleaching stage for both TCF and ECF bleaching sequence (Reeve and Weishar 1991, McDonough 1995, Leroy et al. 2004).

On the other hand, hardwood is the major world pulp wood source accounted about two third of world pulp wood source and which is also the raw material for the only one integrated pulp and paper mill in Malaysia. Hence, the bleachability of hardwood kraft pulp by chlorine-free bleaching, especially O-stage is necessary to be examined. However, O-stage shows relatively lower selectivity as compared to conventional chlorination and alkaline extraction (CE-stage) as first bleaching stage (Smook 1992, Beyer et al. 1999, Suchy and Agryropoulos 2002). As a result, maximizing of O-stage selectivity as well as pulp brightness is important to a chlorine-free bleaching sequence. Thus, the bleaching selectivity of the O-stage should be improved by some modification such as additional of additives or implementing a pre-treatment in the process (Fossum and Marklund 1988, McDonough 1996, Nelson 1998).

In this study, the modification of the O-stage will based on Ng's research as the TCF backbone bleaching stage due to her results had displayed higher selectivity than the conventional O-stage and Op-stages (Ng et al. 2011). However, there is no further research had been done using different chemical pulps. Thus, the effect of modified Op-stage with additives will be examined on the pulp properties such as kappa number, viscosity, selectivity and brightness by using tropical hardwood kraft pulp. Moreover, the structurally and chemically changes in the pulps and extracted residual lignin should be investigated as well in order to verify the fundamental effect of each process on the bleached pulps.

In this study, the effect of the combination of photo pre-treatment in conjunction with/without peracetic acid pre-treatment prior ordinary and modified O-stage which is considered as new approaches for chlorine-free bleaching stages are carried out. The effect of new designed chlorine-free bleaching stages on pulp properties such as kappa number, viscosity, selectivity and brightness will be investigated. Two types of photo pre-treatment which are ultra violet and visible light with different level of energy were selected to be applied. Besides that, the effect of pre-treatments on the residual lignins structure and carbohydrate compositions in the pulp will be examined to verify the changes in lignin and/or pulp that cause the improvement on bleaching selectivity during the subsequent O-stage and improved O-stage.

1.3 Objective

This research study is carried out to achieve the following objectives:

i. To study the effect of ordinary and improved oxygen delignification on hardwood kraft pulp.

ii. To verify and compare the effect of photo, peracetic acid and combination of two pre-treatment (including UV and visible blue light) prior ordinary and improved oxygen delignification.

iii. To identify structural and functional groups changes in pulps and extracted residual lignin that cause the improvement of pulp bleachability.

iv. To compare and identify the best condition among all the modified O-stages for hardwood kraft pulp based on bleaching selectivity and paper properties.

CHAPTER 2 LITERATURE REVIEW

2.1 An overview of pulp bleaching

In order to produce pulp and paper with higher brightness, bleaching process is mainly introduced by either eliminating the lignin or altering its structure from chromophoric to non-chromophoric lignin (Dence and Reeve 1996, Sjöström 1993). Mechanical pulp and semimechanical pulp are basically bleached by using lignin-preserving bleaching methods whereas chemical pulp is bleached by using lignin-removing bleaching methods. Lignin preserving bleaching works by altering the chromophoric structures in the lignin without dissolving the lignin (Casey 1981, Smook 1992, Sjöström 1993). These applications mostly are used for the newspapers and magazines. However, the brightness of these products commonly is not stable because it will regenerate the chromophoric groups when exposure to light and air due to autoxidation (Agarwal et al. 1999, Sippola and Krause 2005). Lignin removing bleaching reacts by dissolving completely the lignin and eliminating it through washing. Pulp for production of tissue paper and printing paper usually used this bleaching method in order to attain high brightness. Thus, the brightness stability will be increased by lignin removal bleaching as well as the brightness stability of the products (Casey 1981, Smook 1992, Dence and Reeve 1996).

In general, instead of one bleaching stage, a full bleached pulp can only be achieved by applying several consecutive bleaching stages. Between 1900-1930s, multi stages of bleaching has been done by using chlorine (C-stage) and followed by an alkaline extraction stage and then, ended with a hypochlorite stage (CEH-stage), which removes 70-90% of the lignin remaining in an unbleached pulp (Tench and Harper 1987, Van Lierop et al. 1989). The fast growing of C-stage is due to the relatively low

operation cost and high selectivity in removal of residual lignin with less carbohydrates degradation. Even as early as 1990, approximately 90% of bleached pulp is produced by chlorine bleaching (Sjöström 1993, Reeve 1996).

However, the chlorination stage (C-stage) creates extremely poisonous and persistent by-products, such as dioxane, chlorinated dioxins, furans, polychlorinated biphenyls and other organic compounds (as shown in Figure 2-1), which are extremely harmful to the environment and human health (Casey 1966, Nelson 1998, Bajpai 2005). Polychlorinated dioxin and furans actually represent the backbone structure of dibenzo-p-dioxin (PCDDs) and dibenzofuran (PCDFs) as shown in Figure 2-1.

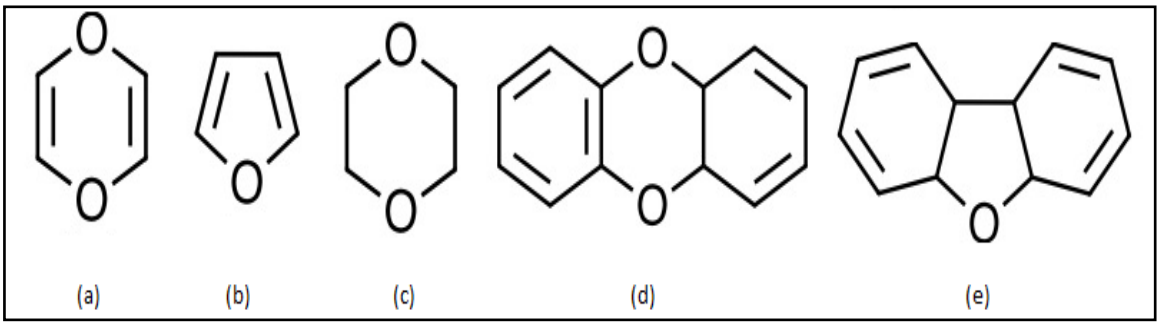

Figure 2-1 Chemical structures of (a) dioxin, (b) furan and (c) dioxane, (d) general structure of dibenzo-p-dioxin and (e) dibenzofuran.enzo-p-dioxin (Bajpai 2005).

Dioxins and furans are known as carcinogen and they leave detectable residuals in the chlorine based bleached product (McDonough 1995, Nelson 1998). As a result, many researches have been carried out to develop alternative bleaching process to minimize the formation of organo-chlorines. In order to reduce the threat to the environment due to employment of elemental chlorine in bleaching process, there are two alternatives in the current bleaching processes:

(i) Elemental chlorine free (ECF) bleaching - The replacement of chlorine dominantly by chlorine dioxide.

(ii) Total chlorine free (TCF) bleaching – a process that uses mainly oxygen and hydrogen peroxide for bleaching with the absent of any chlorine containing compounds
(Sjöström 1993, Dence and Reeve 1996).

In fact, ECF still shows lower environmentally compatibility if compare to TCF bleaching. However, the ECF bleaching still widely implemented in paper mills as compared to the TCF bleaching due to its efficiency and effectiveness relatively higher on the lignin removal with lesser cellulose degradation (Tench and Harper 1987, Mazumder and Tendolkar 2014, Jesse 2015). Moreover, with the increase of public concern over these environmental problems, increase in demand for chlorine-free bleached pulp and paper products are observed since the late 1980s until now. Hence, the implementation of a totally chlorine-free (TCF) bleaching sequences are widely promoted with the aim of eliminating the use of chlorine-based chemicals in bleaching plants completely (Sjöström 1993, Reeve 1996).

Since TCF bleaching treated pulp without any chlorine-based compound, hence, the effluent discharged has less toxicity in comparison to conventional bleaching. For TCF bleaching, different combinations of ozone (Z), peroxide (P), complexing agents, chelation (Q), acid treatment (A), alkaline extraction (E) stage, including the latest chemicals such as peracetic acids and bio-delignification are considered (Smook 1992, Sjöström 1993, Dence and Reeve 1996). Out of the three main bleaching agents normally applied for a totally chlorine free (TCF) bleaching process—namely, ozone (Z), oxygen (O) and hydrogen peroxide (P)—none of these combinations seem to be able to compete with conventionally chlorine based bleaching stages. As for ozone (Z-stage), the bleaching reaction takes place under the acid medium, therefore, it may probably

decompose into free radicals and induce cellulose degradation and results, in a decrease of pulp strength (Smook 1992, Dence and Reeve 1996, Liebergott 1996).

Oxygen delignification (O-stage) is commonly used as the first bleaching stage to eliminate the bulk of residual lignin from the brownstock. However, the biggest drawback of an O-stage is its relatively low delignification, which is only limited to no more than 50%. Previous studies reported that beyond the limit of degree of delignification, the oxygen delignified pulp shows lower strength properties due to low selectivity between delignification and carbohydrates degradation (Ismail and Guniz 2008, Leh et al. 2008).

Alkaline hydrogen peroxide (P-stage) is generally applied in pulp and paper mills to bleach the mechanical pulp with relatively high residual lignin to high brightness (around 80% brightness). On the other hand, the addition of a final P-stage in TCF bleaching stages can improve the chemical pulp's brightness stability while preserving higher pulp viscosity and pulp strength. This is mainly due to oxygen derived compounds are likely to attack both carbohydrates and lignin unselectively if compared to chlorine counterparts (Parthasarathy et al. 1990, Hosoya 1992, Johansson and Ljunggren1993, Stevens and Hsieh1995).

Since the efficiency of the first stage of bleaching sequence is very important, the low selectivity of TCF bleaching stage will substantially limit its role in pulp bleaching process and finally, it may also restrict the efficiency of bleaching sequences (Parthasarathy 1990, Ahuja 2001). In comparison to the first two bleaching stages of the conventional bleaching sequence, the delignifying ability of TCF bleaching is far lower than the chlorination stage (C) followed by an alkaline extraction (E), which can

eliminate up to 90% of the residual lignin (Casey 1981, Smook 1992, Dence and Reeve 1996). Since chemicals used for TCF bleaching generally have relatively low selectivity, thus, more bleaching stages are required in order to produce full bleached pulp. As a result, TCF sequences are likely to have more yields loss than ECF sequences when the bleaching sequences have the same result in kappa and final brightness. For this reason, the pulp with lower kappa number is required before entering TCF bleaching plant in order to minimize the rate of the cellulose degradation in the subsequent bleaching stages (Casey 1981, Smook 1992, Dence and Reeve 1996).

This indicated that even though TCF shows higher environmentally compatibility than ECF, but in terms of pulp strength, brightness and recyclability, ECF pulp have better pulp properties than TCF pulp. Hence, for pulp millers, higher preference is still given to ECF (Mcdonough 1995, Leroy et al. 2004). Consequently, it has still become a challenge for the researchers to enhance TCF bleaching selectivity by further improving its delignification and minimizing the impact on cellulose deteriorating.

2.2 Oxygen bleaching

Oxygen delignification (O-stage) can be defined as the use of oxygen under high pressure and alkaline medium at high temperature to degrade lignin from the pulp. Commonly, O-stage is used as the first bleaching stage to eliminate the bulk of residual lignin (Sjöström 1981, McDonough 1996, Nelson 1998). Among all the chlorine-free bleaching agents, O-stage plays an important role in developing TCF bleaching process. However, in comparison to conventional bleaching (chlorination stage followed by an alkaline extraction), like most of the TCF bleaching process, O-stage shows relatively lower selectivity, which is indicated by low delignifying power but more extensive degradation of carbohydrates (Barroca et al. 2001, Suchy and Agryropoulos 2002). Generally, the removal of lignin by an O-stage is limited to 50% or lower which is depending on the pulp. Beyond that limit, both lignin and carbohydrates are degraded unselectively, resulting in a relatively weak pulp with lower pulp brightness and pulp strength. Thus, the selectivity of an O-stage contributes the main influence on TCF bleaching performance (Sjöström 1981, Smook 1992).

2.2.1 Brief history and development of O-stage

In 1867, oxygen gas was spotted as a potential bleaching agent and first introduced by Joy and Camphell. In 1915's, Mueller has introduced an oxygen pressurised method with the addition of the alkaline earth metal hydrate to bleach the pulp. In 1960s, Robert and co-worker were found out the additional magnesium salts during O-stage can preserve the pulp strength properties (McDonough 1996, Nelson 1998, Steffes et al. 1998). Thus, oxygen was first introduced as a bleaching agent in the late 1960s and early 1970s to act as extended delignification prior to a conventional bleaching sequence (McDonough 1996, Nelson 1998). Nowadays, O-stage still remains not well commonly implemented in pulp mills. The main reason O-stage less favourable for bleaching

process is due to lignin and cellulose was attacked unselectively, at the same time, leading to sharp decreases in pulp viscosity as compared to conventional chlorine based bleaching. So, this will limit the lignin removal capabilities of oxygen delignification not beyond than 50% to avoid the serious cellulose degradation (Smook 1992, Reeve 1996, Nelson 1998).

Changes in the environmental regulations and social awareness have noticeably transformed the bleaching trend in pulp and paper mills. In order to minimise the use of chlorine based compounds, O-stage is first introduced in pulp mill as a pre-delignification stage in 1970 (McDonough 1996, Nelson 1998). The employment of O-stage could be use of an extended delignification after pulping and the recycling of O-stage's effluent. Thus, it is capable of replacing the elemental chlorine bleaching stage and reducing any environmental impact of the bleach plant (McDonough 1995, Nelson 1998, Barroca et al. 2001).

The O-stage under alkaline conditions is developed to between pulping and traditional chlorination stage (by replacing the chlorination and alkaline extraction stage (CE-stage) and chlorination–alkaline extraction–hypochlorite (CEH-stage)). It is the first move in the bleaching revolution with the aim to reduce the consumption of chlorine-based chemicals during the subsequent bleaching stage. Hence, the bleaching sequence is shortened from CEDED to OCED and it also improves the resultant pulp brightness with acceptable pulp properties (Tench and Harper 1987, Dence and Reeve 1996). A lower kappa number of unbleached pulp following O-stage given the result in a less chemical charge is required to bleach the pulp. Thus, it is capable of saving chlorine based chemical charges and others chemical requirement to achieve the targeted brightness.

The first commercial oxygen delignification plant was started up at the Sappi kraft mill at Enstra, South Africa (1970) when technology are developed well enough to establish pressurized operations, the separation and purification of oxygen from atmosphere, and the discovery of chemicals that could function as carbohydrate protectors (McDonough 1996, Nelson 1998). However, the installation of O-stage in pulp mills has slowly increased when the beneficial effect of magnesium salts is discovered. After that, single and two-stage medium O-stages are developed and available in the market. The total worldwide production capacity of the oxygen delignified pulp is increased up to 120,000.00 tons per day in the year 1995 (Dence and Reeve 1996, SANH 1996). Furthermore, this rapidly growth is likely continued in nowadays.

Currently, the main benefits of O-stage are an efficiency bulk delignification process, economy process, energy savings and an environmental feasible process. Even though the system demands a high capital cost, the operating cost on bleaching agent and waste recovery system is lower than the chlorine based plants (Tench and Harper 1987, Barroca et al. 2001). Moreover, the discharge from an O-stage can be recovered in the chemical recovery system to reduce the bleach plant effluent load and increase the energy recovery. Consequently, the environmental impact from colour, chemical oxygen demand (COD), adsorbable oxygen halides (AOX) and biological oxygen demand (BOD) in bleach plant effluent are reduced as well (Smook 1992, Reeve 1996, Nelson 1998).

2.2.2 Process variables of O-stage

Oxygen gas is a weak oxidizing agent in normal condition but it can be promoted in alkaline medium with high temperature and pressure in the reactors. The key parameters which affect the optimising an O-stage are temperature, reaction time, chemical charge, oxygen pressure, and pulp consistency (McDonough 1983, Agarwal

1997, Barroca et al. 2001). Effects of each variables of O-stage including the initial kappa number of pulp should be understood clearly to get desired mechanical and optical properties of pulp. According to many studies, continuing increase the operation temperature, alkaline charge and reaction time will substantially accelerate the rate of delignification and carbohydrate degradation in the bleaching process, especially beyond the limit and alkaline charge are exhausted (McDonough 1983, Agarwal 1997, Barroca et al. 2001). The higher temperature applied in the O-stage enhances the rate of delignification as more chemical will impregnation into the fibre wall and react with lignin (Smook 1992, Agarwal 1999, Doğan and Gürüz 2008).

On the other hand, the effect of oxygen pressure and consistency are normally insignificant in comparison to the effect of alkaline charge and temperature on oxygen delignified pulp. The oxygen pressure is necessary to impregnate the oxygen easily into the fibre wall. The low solubility of the oxygen in the alkaline medium will increase the difficulty of the oxygen transferred across the gas-liquid interface surrounding the fibres and diffuses into the fibre wall. Lower consistency will lead to a moderate slowing down of both lignin and carbohydrate degradation, as a result, it will associate decrease in alkaline concentration and less penetration of oxygen into high thickness of liquid layer on the fibre surface (McDonough 1983, Nelson 1996). Thus, the low consistency generally has higher chemical consumption and low extents of delignification than the high consistency condition.

A lower kappa number of unbleached pulp following O-stage given the result in lesser chemical charge is required to delignify the pulp. Along the O-stage, the degradation two types of lignin are paralleled together with the reaction time exhibits two distinct stages at fixed alkaline charge. The first type lignin will be removed within the

first ten minutes in a rapid initial phase, while second type lignin is removed in a slow and bulk final phases in the rate that is proportional to the reaction time and the amount of lignin remaining in the pulp as shown in Figure 2-2. The kappa number reduction can be further reduced to any desirable level with the optimum increase in the chemical charge, temperature, oxygen pressure and reaction time. However, the delignification process appears to be stopped when a limitation on kappa number is reached (Olm and Teder 1979, McDonough 1983, Barroca et al. 2001).

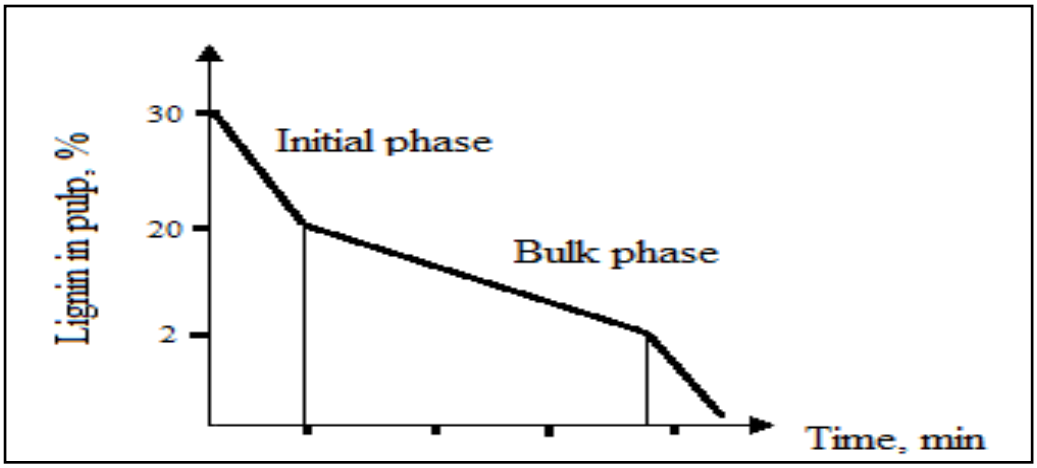

Figure 2-2 Effect of time on lignin during the oxygen delignification (Dence and Reeve 1996).

2.2.3 Oxygen chemistry reaction in O-stage

The understanding of chemistry and fundamental process between oxygen reactive species, lignin and carbohydrates may assists to enhance the efficiency of an O-stage and provide a logical framework for predicting the effects of key changes during the system. The procedure of the O-stage has been examined using lignin model compounds as well as based on structural changes in both residual and dissolved lignin. Oxygen dissolved in alkaline medium will decompose into reactive species from molecular oxygen and attacks electron-rich sites on both lignin and carbohydrates in the delignification process (Smook 1992, Dence and Reeve 1996). Molecular oxygen share their tendency to react with suitable substrates and transform into reactive species such as superoxide anion

radical and singlet oxygen due to the biradical nature of oxygen with unpaired electron (•O-O•) (Wasserman 1979) .

The initial step began by the reduction of molecular oxygen to generate superoxide anion radicals (O_2•$^-$) which can react with hydrogen ion to form hydroperoxy radicals (HOO•) as shown in Figure 2-3. Among those reductive, superoxide radicals and hydroperoxy radicals have higher attraction for electrons where tend to accept an electron. When the pH of the medium is sufficiently high, the superoxide radicals and hydroperoxy radicals were readily to accept another electrons to form hydroperoxy radicals (HOO•) and hydrogen peroxide (H_2O_2) in the second reduction step of the oxygen. After hydrogen peroxide receive an electron to form like hydroxyl radicals (HO•), it can finally further to form hydroxide ion or water. The reactive species like hydroxyl radicals (HO•), hydroperoxy radicals (HOO•) and superoxide anion radical (O_2•$^-$) act as electrophilic agent while hydroperoxide anion (HOO^-) and hydroxyl anion (HO^-) as nucleophilic agent during the delignification process (Gierer et al. 1991, Sjöström 1993, Guay et al. 1999, Sixta et al. 2006).

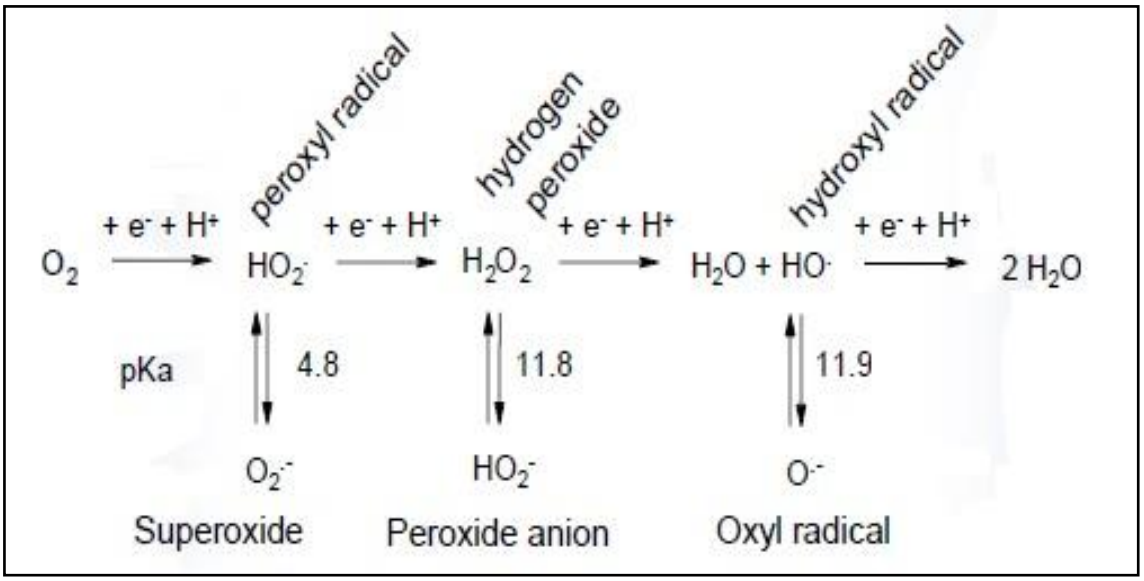

Figure 2-3 The stepwise reduction of oxygen (Sixta et al. 2006).

Lignin structure with free phenolic hydroxyl groups is one of the predominant sites to initiate the reaction with the reactive species. The reactive species primarily attack aromatic lignin unit to induce the cleavage of the aromatic ring and side chain scission as shown in Figure 2-4. In this reaction, a phenoxy radical is formed together with a hydroxyl radical and superoxide. In the subsequent reaction, the phenoxy is oxidised and degraded with formation of carboxylic acid groups which are ionised and contribute to water solubility under the alkaline condition. Hence, the muconic acid and carbonyl structures are formed as shown in Figure 2-4 (Gierer 1993, Dence and Reeve 1996, McDonough 1996).

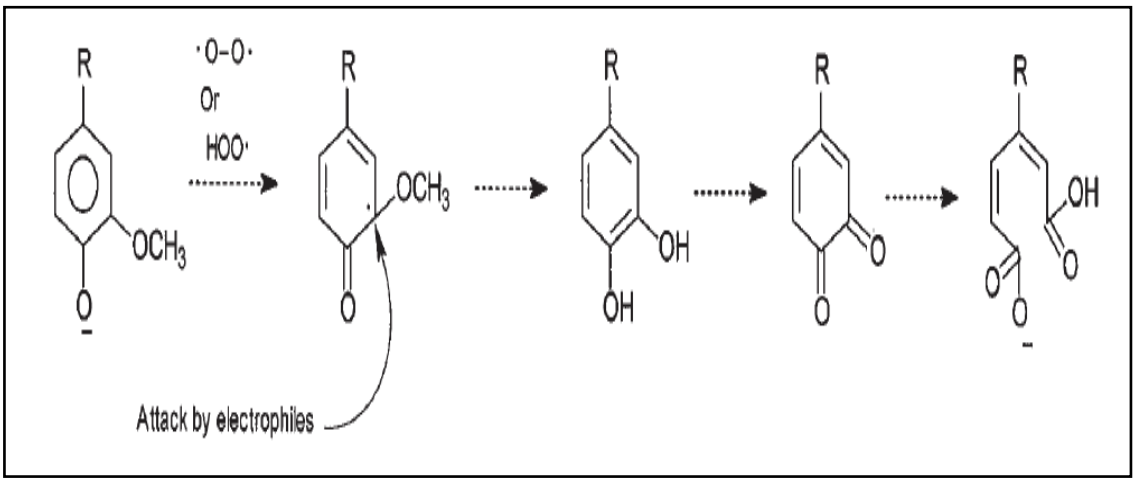

Figure 2-4 Major reaction product of lignin via the phenoxy radical by O-stage-alkali treatments (Sjödin et al. 1994).

The hydroxyl radical is identified as a strong oxidizing agent (standard redox potential E^0 ~ 2.3 V in neutral aqueous medium) and proposed to be the actual species responsible for lignin and cellulose degradation. After the ionization in alkaline medium, hydroxyl radical is readily react with the aromatic or double bond functional groups due to its electrophilic character (Sixta 2006). Thus, O-stage process can summary as initiation, propagation and termination as in the following Equations 2-1 to 2-5: