CHARACTERIZATION OF RECOVERED BLACK LIQUOR AND ISOLATED LIGNIN FROM OIL PALM EMPTY FRUIT BUNCH SODA PULPING FOR SEMICHEMICAL AND CHEMICAL PULPS

by

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LIST OF ABBREVIATIONS

AQ	Anthraquinone
NaOH	Sodium hydroxide
Na_2S	Sodium sulfide
Min	Minutes
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
L:M	Liquor: Material

LIST OF SYMBOLS

Ws	Weight of sample
A_c	Chromatography area of component peak
W_s	Weight of internal standard, g
A_s	Chromatography area of internal standard peak
W_c	Weight of component, g

PENCIRIAN LIKOR HITAM TERPULIH SEMULA DAN LIGNIN TERASING DARI PEMULPAAN SODA UNTUK PULPA SEMIKIMIA DAN KIMIA TANDAN BUAH KOSONG KELAPA SAWIT

ABSTRAK

Likor hitam selepas proses pemulpaan dalam kilang pulpa, mengandungi hasilan degradasi lignin dan karbohidrat serta komponen bukan organik. Keputusan menunjukkan pH dan sisa alkali likor hitam meningkat dengan peningkatan jumlah alkali yang digunakan semasa proses pemulpaan. Sementara, kelikatan likor hitam lebih bergantung pada degradasi lignin. Peningkatan cas alkali menghasilkan hasil pepejal kering likor hitam yang lebih tinggi. Penambahan antraquinone (AQ) ke dalam proses pemulpaan menunjukkan penstabilan karbohidrat dan delignifikasi yang lebih baik. Analisis daripada Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) menunjukkan lignin terasing mengandungi hanya sedikit komponen bukan organik. Manakala, analisis Gas Chromatography (GC) menunjukkan likor hitam dengan AQ mengandungi kandungan karbohidrat yang lebih rendah daripada likor hitam tanpa AQ. Hasil lignin terasing mencapai tahap maksimum pada pH 2 dan keputusan setanding boleh juga diperoleh dengan pH 4.5 diikuti pemanasan selama sejam. Namun, proses karbonasi tidak menunjukkan peningkatan hasil pengasingan lignin yang signifikan. Analisis kumpulan berfungsi pada lignin terasing dengan Frourier Transform Infrared Spectroscopy (FT-IR) tidak menunjukkan perbezaan ketara antara lima jenis pengasingan lignin. Analisis juga menunjukkan pepejal kering likor hitam mempunyai kumpulan berfungsi kurang daripada lignin. Analisis daripada Gas Chromatography-Mass Spectrometry (GC-MS) menunjukkan komponen seperti benzaldehyde, 4-hydroxy-3,5-dimethoxy- and ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl) boleh didapati dalam setiap lignin terasing

CHARACTERIZATION OF RECOVERED BLACK LIQUOR AND ISOLATED LIGNIN FROM OIL PALM EMPTY FRUIT BUNCH SODA PULPING FOR SEMICHEMICAL AND CHEMICAL PULPS

ABSTRACT

The spent liquid after the pulping process in pulp mill, generally known as black liquor contains degraded lignin and carbohydrates and inorganic compounds. Results showed that the pH and the residual alkali of black liquor increased with the increase of total alkali used during the pulping process whilst the black liquor’s viscosity mainly depends on the dissolved lignin. The increase of alkali charge resulted higher dry solid yield due to the increase of both inorganic compounds and dissolved organic compounds. The addition of anthraquinone (AQ) in the pulping process showed an improved carbohydrates stabilization and better delignification. Analysis by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) showed that the isolated lignin contains traces of inorganic compounds, while Gas Chromatography (GC) analysis showed that black liquor with AQ had lesser carbohydrates content than black liquor without AQ. Optimum lignin precipitation was obtained at pH 2 and comparably result could be obtained at pH 4.5 followed by 1 hour heating. However, the carbonation process did not show significant improvement on lignin precipitation. The analyses of functional groups by Frourier Transform Infrared Spectroscopy (FT-IR) showed not much different among five types of isolated lignin. Besides, the black liquor dry solid sample showed less functional group than isolated lignin. The analysis by Gas Chromatography-Mass Spectrometry (GC-MS) showed that typical compounds such as benzaldehyde, 4-hydroxy-3,5-dimethoxy- and ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl) were found in isolated lignin.

CHAPTER 1

INTRODUCTION

1.1 Introduction

The plantation of oil palm (*Elaeis Guineensis*) is growing rapidly in Malaysia since early 1970s due to the government's policy, the Second Malaysia Plan (RMK-2), which encouraged the diversification of the major country's major crops. The great establishment of oil palm industry was also accompanied by the generation of abundant oil palm biomass residues such as trunks, fronds, shell, empty fruit bunch (EFB) and mesocarps (Husin et al., 1985). In order to overcome the problem such as curbing pest breeding in the plantation and open burning of the oil palm residues, owing to the left and unused biomass, many researches had started to study the feasibility of the utilization of the material by converting it into value added products including pulp and paper (Guritno et al., 1994; Akamatsu et al., 1987; Khoo & Lee, 1991; Laurence et al., 1996; Wan Daud et al., 1998).

Among the biomass, EFB shows a high potential as a promising alternative raw material for pulp and paper industry. Many studies had been carried out to produce pulp and paper by using environmentally compatible processes such as sulphur free pulping and chlorine free bleaching in order to establish sustainable development in pulp and paper industry (Akamatsu et al., 1987; Khoo & Lee, 1991; Wan Daud et al., 1998; Law & Jiang, 2001; Tanaka & Wan Daud, 1999).

In regards of this achievement, Malaysian's government foresees the pulp and paper industry as an important industry in the near future. However, the development of this industry is considerably slow due the obstacle related to the environment conservation. The plan of setting up the world's first oil-palm based pulp and paper mill by using caustic soda pulping process, cost around RM 80 million, with the capacity 25, 000 tonnes of pulps a year was expected to be launched on August 2004 at Kunak, Tawau, Sabah (Business Times, 2003). Besides, a joint venture between the government and the private sector in setting up a pilot plant at the Ulu Sebol Palm Oil Mill in Kulai, Johor with a capacity 7,500 tonnes of pulps a year with the estimated cost of RM 30 million was also expected to be fully operated in 2004 (Business Times, 2002). However, establishment of both mills going to be employed failed to continue and thus the efficiency recovery system of the black liquor also failed to be evaluated.

Black liquor is the spent liquid after the pulping process from the pulp mill. It is very complex, contains high alkalinity and high dissolved solids such as lignin residues, degraded carbohydrates and inorganic constituent (Wallberg, 2006; Sjostrom, 1993). Although the pulping chemical in the highly proposed soda pulping process is only sodium hydroxide (with or without anthraquinone as catalyst), the discharging of this spent liquor/black liquor into the downstream without proper treatment will definitely bring serious water pollution in term of biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), colour unit, pH, odour and etc. (Smook, 1992).

Due to the reason mentioned above, there is a need to solve the black liquor problem for any future advancement in pulp and paper industry in Malaysia. Usually for conventional high capacity kraft mills (1000 tonnes per day or more), black liquor from kraft pulping of hardwoods and softwoods can be incinerated economically for energy recovery, inorganic chemicals recovering and combustion of organic constituents in order to minimize effluent load by installing recovery system (Gullichsen & Fogelholm, 2000; Saroha et al., 2003). However, for the production of non-wood pulp, it is not practical to be established as high capacity pulp mill because of insufficient of raw materials supply. Furthermore, the silica content of non-wood fibers is considerably high and thus the water-soluble silicate ions will cause the scaling on the transfer surfaces in the evaporator during the black liquor concentration process (Hammett et al., 2001; Saroha et al., 2003; Myreen, 2001).

Many studies had found that soda pulping is the most suitable for non-wood pulping especially oil palm EFB (Law & Jiang, 2001; Tanaka & Wan Daud, 1999), but black liquor resulting from the soda pulping is difficult to be recovered as compared to kraft pulping by the concentration/ combustion process (Ken Maddern, 2003; Feng & Alen, 2001). Even though large scale non-wood paper mills can afford the installation of the recovery system and able to obtain sufficient supply of fiber, but they might encounter some technical problems when trying to use increased level of non-wood fiber (Hammett et al., 2001).

Since the production of pulp and paper from oil palm EFB is infeasible and not advisable to be established in a high capacity pulp mills due to economic and transportation aspects, so it indicated that a suitable method is required to treat the black liquor before discharging into the downstream. The degraded lignin in black liquor is the main contributor of both BOD and COD. Based on the report by Lora & Escudero (2000), the level of COD of the black liquor which had been treated to recovery and separated the degraded lignin was reduced about 50%. The filtrates from the recovery process contain mostly sugars and organic acid and thus, could be treated easily by biologically treatment before discharging into the downstream (Lora & Escudero, 2000; Smook, 1992; Sjostrom, 1993).

The characterization of softwoods and hardwoods black liquor had been done extensively since mid 1970s (Lowendahl et al., 1976; Samuelson & Sjoberg, 1978; Alen et al., 1985b, 1985a; Niemala, 1988, 1990, 1991; Dong & Fricke, 1995; Alen & Siistonen, 1998; Niemala & Alen, 1999). The black liquor from the pulping of non-wood fibers such as reed canary grass, sugarcane baggasse, wheat straw have been investigated lately (Lora & Escudero, 2000; Baudel et al., 2005; Feng et al., 2001, 2002). However, only little works had been done on the black liquor from EFB pulping process. The studies carried out by Sun et al. (1999) and Mohd Ibrahim & Chuah (2004) only concentrated on lignin isolation from oil palm black liquor and minor on characterization of lignin. Both studies showed that acidification by mineral acid to pH 2 gave a desirable yield of lignin from black liquor. However, the yield (1.0 – 1.3g/ 100 ml) is still much lower compared to yield of lignin obtained from (4.5 – 6.5 g/ 100 ml) kraft pulping.

The lignin recovered from the black liquor is widely recognized to be used as binder for adhesives or as additive such as oil well drilling additives, concrete additives, agricultural chemicals and industrial binders (Gargulak & Lebo, 2000), turning the lignin-rich black liquor to value-added products which will assist the development of pulp and paper industry in Malaysia. Hence, the recovery of the black liquor/ lignin not only reduced the effluent problems, it will also become additional income for small pulp millers. However, characterization of black liquor/ lignin from oil palm EFB soda pulping processes has to be carried out before it can be used for commercial purposes.

1.2 Objective

In this study, an attempt was made:

- To characterize black liquor from various pulping conditions of oil palm EFB
- To isolate lignin from black liquor by acidic precipitation
- To investigate lignin which is obtained by various precipitation method

CHAPTER 2

LITERATURE REVIEW

2.1 The Impact of Pulp and Paper Industry toward the Environment

The pulp and paper industry is recognized as one of the world most highly polluting industries (Ritchlin & Johnston, 1999). The emissions from pulp and paper mills either air or water gives a serious impact on environmental quality that eventually affects the health of both human and ecosystems. The liquid discharge into the downstream usually generated from various stages of pulping and bleaching process. The effluent contains compounds such as resin acids, unsaturated acids, chlorinated phenolic, chlorinated dioxins and furans which are toxical to human bodies. In addition, the major air pollutants include fine and coarse particulates, sulfur dioxide, nitrogen oxides, reduced sulfur gases and volatile organic compounds. The reduced sulfur gases give a nuisance to the people with its odour (Smook, 1992; Ritchlin & Johnston, 1999). Therefore, the pulp and paper industry is always under constant pressure to be in compliance to the environmental regulations. So, environmental issues have always been the key role in the development of pulp and paper industry (Young & Akhtar, 1998).

Pulping is a process where the wood chips or other fibrous raw materials are ruptured mechanically, thermally, chemically or combinations of these treatments into a fibrous mass which known is as pulp (Smook, 1992). The conventional pulping processes can be classified as mechanical, chemical or hybrid pulping processes. The source of wood might come from softwoods or hardwoods while fibrous raw materials are agricultural residues, natural growing plants and cultivated fibre crops and each example is shown in Table 2.1.

Table 2.1: Classification of Non-wood Fibrous Raw Materials

Type	Material
Agricultural residues	Cereal straws (wheat, barley, rice, corn, rye, oats) Sugarcane bagasse Pruning residues (grapevines, fruit trees) Oil palm residues (empty fruit bunches, palm fronds) Textile residues (hemp, flax, jute, cotton)
Natural growing plants	Esparto grass, hay, ray, ryegrass, bamboo, cane
Cultivated fibre crops	Kenaf, miscanthus, paper making sorghum

(Lora, & Escudero, 2000)

Mechanical pulping is a process of shredding and defibring the wood chips or fibrous raw materials into shorter and stronger fiber (Smook, 1992; Casey, 1980). Mechanical pulping is the least environmental hazardous process and has the advantage of producing a very high pulp yield compared to other processes. Mechanical pulping process also causes lower level of water pollution and less consumption (45, 000 – 68, 000 litres/ tonne) compared to chemical pulping (159, 000 – 204, 000 litres/ tonne). In other words, low level water usage means less effluent discharge that contains degraded lignin, organic compounds and inorganic compounds but indeed effluent from mechanical pulping contains very little of these substances. However, mechanical pulping has the disadvantages of being a major user of electrical energy and producing generally lower grade pulp (Stanley, 1996).

Chemical pulping is a process where the wood chips or fibrous raw materials are cooked in an aqueous solution at elevated temperatures and pressure with appropriate chemicals. Chemical pulping is chemically separating the fibrous fiber into pulps by degrading about 90% of the lignin from the materials and retaining most of the cellulose and hemicelluloses. The chemical pulping methods can be classified into two major principles namely; alkaline such as kraft process and soda process and acidic such as sulfite and bisulfite process. The kraft process is a modification of the soda process which utilizes sodium hydroxide (NaOH) with the addition of sodium sulfate (Na_2SO_4) into the cooking liquor system (Sjostrom, 1993; Smook, 1992). Sulfite pulping is a solubilization of lignin which has removed from cellulose as salts of lignosulfonic acid using mixtures of sulfurous acid (H_2SO_3) while bisulfite pulping using bisulfite ion (HSO_3) (Casey, 1980; Smook, 1992). Besides, sulfite pulping also can be carried in neutral and alkali medium and known as neutral sulfite process and alkaline sulfite process (Smook, 1992).

Kraft pulping is always associated with severe environment pollution especially the air pollution. The air pollution from the kraft pulping is a major concern with the emission of sulphur gases into the atmosphere with a rate of 0.3-3 kilograms per metric tonne (kg/t) of air-dried pulp (ADP) (World Bank Group, 1998). The four reduced sulphur gases are hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide. The obnoxious odour of the gases even released from the advanced kraft mills. All the gases have extremely low odor thresholds, which indicated that long term exposure to these gases, the balance of ecosystem and even human health will be seriously interfered (Smook, 1992; Casey, 1980; Biermann, 1996).

Both kraft and sulfite pulping processes emit the gas of sulfur oxides (SO_2) but the amount of emission from kraft pulping is not as much as sulfite pulping. More sulfur oxides are generated from sulfite mills at about 5 kg of SO_2/ tonne than 1-3 kg SO_2/ tonne from kraft mills (Smook, 1992; Stanley, 1996). Other pollutants include such as particulate matter, nitrogen oxides and volatile organic compounds (VOCs) from the black liquor oxidation process (World Bank Group, 1998). The major air pollutants and their effects are summarized in Table 2.2.

Table 2.2: Air Emissions from the Pulp and Paper Industry

Pollutant	Source	Effects
Fine particulates	Soda fume from the kraft recovery furnace	Affect respiratory system
Course particulates	"Fly ash " from hog fuel and coal-fired boilers	Affect respiratory system
Sulfur oxides	Fuel combustion and pulping process especially sulfite mill	Acid rain
Hydrogen sulphide (reduced sulfur gases)	Kraft process	Rotten egg smell
Volatile organics	Noncondensible gases from digester relief & spent liquor evaporation	Toxic effects to the formation of ozone
Carbon dioxide	Fuel combustion	Greenhouse effect
Nitrogen oxides	From all combustion processes	Photochemical impact in the atmosphere
Chloroform	Chlorine bleaching	Toxic, possible carcinogen
Other organochlorines	Chlorine bleaching	Some highly toxic

(Smook, 1992; Stanley, 1996)

The impact of discharging the effluent discharged from the chemical pulp mills into the receiving water has roused the awareness of public and thus, exerts pressure on the pulp and paper mills. The effluent from pulping process, also known as black liquor is considered highly hazardous to the environment due of alkalinity and high dissolved solids such as lignin residues, degraded carbohydrates and inorganic constituent if discharged into downstream without proper treatment (Smook, 1992; Stanley, 1996; Wallberg et al, 2001). The organic pollutants in effluents such as cellulose fiber, carbohydrates, starch and hemicellulose (or the organic acids resulting from their breakdown), which degraded during the pulping process are the main contributor to biological oxygen demand (BOD) and chemical oxygen demand (COD). According to World Bank Group (1998), the production of 1 tonne of air dried pulp, generated 10-40 kg of BOD and 20-200 kg of COD. Besides, considerable high total suspended solid (10-15 kg per tonne air dried pulps) also has been reported.

The high discharge of COD consumes oxygen depletes that actually available to fauna and flora, thus damaging the ecosystem near effluent discharged. High levels of suspended solids from the pulp mill effluent can also cause problems of both water opacity and blanketing of river or lake beds. Severe blanketing may also result in anaerobic decomposition under the blanket where hydrogen sulfide will be released into the aquatic ecosystem. Organic solids can also absorb many of the toxins presents in mill effluents, such as resin and fatty acids and heavy metals. This can have long-term effects over a wider area as a result of bioaccumulation and transportation through the food chain (Stanley, 1996).

In order to meet with increasingly stringent environmental regulations, organosolv pulping had been developed. Organosolv pulping is a chemical pulping which carried out by using organic solvent such as alcohols, organic acids and organic chemicals such as ester and phenol to aid in the removal of lignin from materials (Young & Akhtar, 1998). Many studies had verified that the properties of the pulps from organosolv pulping are comparable to the kraft pulps (Dahlmann & Schroeter, 1990; Funaoka & Abe, 1989; Gottlieb et al., 1992; Young, 1989). The introduction and development of organosolv pulping is aimed to reduce the environment pollution by improved pulping process. Since organosolv pulping using organic solvent and sulphur-free and thus, reduce the air pollution problems.

The simplest organosolv pulping process is the non-catalyzed solvent- water pulping which the earliest research on organosolv pulping was proposed by Kleinert & Tayenthal (1931). It is a process which raw materials, organic solvent and water are heated in a pressure vessel without any added catalysts. After decades of researches, the non-catalyzed solvent-water pulping emerged a better process named Alcell (Alcohol-Cellulose) process. Alcell process usually use methanol or ethanol as the pulping agents among the alcohol groups. Since Alcell process using only organic solvent and water, the solvent recovery is easily to be done by evaporating the spent liquor and thus, conserve environmental quality.

However, due to the high volatility of the methanol and ethanol, study was carried out by employing acetic acid as the organic solvent. Nimz & Casten (1985) introduced Acetosolv process which used acetic acid as cooking liquor and added mineral acids as a catalyst. Nimz et al. (1989) continued their research in acetosolv at high temperature but without catalyst and named it as Acetocell. However, the chemical recovery system for Acetosolv and Acetocell pulping liquor by recovering the acetic acid and water was a costly process and hence, discouraged pulp mills to employ.

Several years later, organosolv pulping with sulfur compounds named alkaline sulphite anthraquinone-methanol process (ASAM) pulping had been developed (Kordsachia & Patt, 1988a; Kordsacha et al., 1992). However, the ASAM recovery system is more complicated than a kraft system because it required additional components apart than the usual kraft components such as carbonator to strip out hydrogen sulfide, incinerator to convert H_2S to sulfur dioxide, sulfur dioxide scrubber and carbon dioxide multistage fortication facility (Faix et al, 1990). Furthermore, energy and chemical cost are higher for its recovery system and is not totally odour free since ASAM still use sulfur compounds (Young & Akhtar, 1998).

The MILOX pulping is a three-stage sequence in which peroxyformic (a mixture of formic acid and hydrogen peroxide) acid stage is followed by pulping in formic acid and then again with peroxyformic acid (Laamanen et al., 1986, 1988; Poppius et al., 1987; Sundquist, 1996). MILOX pulping is a promising pulping process but also face the similar problem with its counterpart, a difficulty of recovering the solvent economically. This is due to the spent pulping liquor generated from MILOX pulping contains water, formic acid and acetic acid (dissolved from hardwoods fiber during pulping) which these three components form a ternary azeotrope. Furthermore, water and formic acid form a binary and thus, separating these three components is a costly process (Koljonen et al., 1992; Sundquist & Poppius-Levlin, 1992; Poppius-Levlin et al., 1993; Sundquist, 1996).

Due to the awareness towards the negative impact of kraft mill's effluent to the environment recently, soda pulping started to regain its popularity among the pulp mills especially non-wood based pulp mills after it had been abandoned since 1930s (Smook, 1992; Biermann, 1996). Actually, soda pulping was the first recognized chemical pulping method as early as in 1850s before it was overtaken by kraft pulping. The increased popularity of kraft process was basically due to its cheaper makeup by using sodium sulfate (saltcake) to replace sodium carbonate (soda ash) which used in the recovery furnace of soda pulping. Besides, kraft process also greatly accelerated delignification and resultant stronger pulps (Smook, 1992).

The chemical recovery system of soda pulping is essentially the same as of kraft pulping. Soda pulping does not involve the use of sulfur compounds to facilitate delignification, thus the emission of total reduced sulphur (TRS) related odour problem associated with kraft pulping does not occur. In other words, soda mills do not have to install the extensive TRS control system which is generally required by kraft mills to reduce the TRS emission (Green et al., 1992). However, black liquor resulting from soda pulping is difficult to be recovered as compared to kraft pulping by the concentration/combustion process (Ken Maddern, 2003; Feng & Alen, 2001). So, a better alternative is required to solve the black liquor from soda pulping, apart from chemical recovery system.

Apart from pulping process, the effluent generated from bleaching process also had been identified as a contributor of the most significant pollutants to the environment particularly the bleach plant of kraft pulp mill. Bleaching is required for the production of the high grade paper which the whiteness or brightness of the paper is necessary. Brightness is a test of its paper ability to reflect monochromatic light in comparison to a known standard, magnesium oxide which has (96% brightness by the reflectance of blue light) (Casey, 1980; Biermann, 1996). In order to produce high brightness chemical pulps, bleaching is required to eliminate the residual lignin with chemical agents. The delignifying bleaching process produces pulps with highly stable or permanent brightness (Sjostrom, 1993; Biermann, 1996). Bleaching process usually performs in a sequence of several stages due to the complexity of lignin nature which reacts differently with different bleaching chemicals. Thus, the employment of different bleaching agents in a sequence enable to reduce the amount of chemical required and also enhance the delignification of lignins while minimizes the cellulose degradation (Smook, 1992; Biermann, 1996).

Unbleached kraft pulp is dark brown in colour. This is due to the structure of residual lignin of kraft pulp is highly modified or recondensed during the pulping process (Addleman & Archibald, 1993). Unbleached kraft pulp mainly requires a series of bleaching processes which contain chlorination stage (C) or other chlorine containing bleaching stage to achieve high brightness (70-92%) (Biermann, 1996). However, the effluent discharged from the mentioned bleached plant has been recognized of its content of highly toxic chlorinated organic compounds especially polychlorinated dioxins and furans. Most of the compounds to the human bodies for a period of time will also cause other health risks such as endocrine system disruption, birth defects, immunity system disorder and reduced fertility (Stanley, 1996; Smook, 1992; Nelder, 1995).

Elemental Chlorine Free (ECF) and Totally Chlorine Free (TCF) had been established as a consequence of increasing pressure from the public towards conventional chlorination bleaching process. The ECF bleaching sequence is similar to the usual bleaching process except the first stage of bleaching, chlorination (C) is replaced with chlorine dioxide, ClO_2 (D). The substitution of gaseous chlorine (elemental chlorine) as a bleaching agent with chlorine dioxide reduced the level of chlorinated organics or organochlorines (measured as AOX – adsorbable organic halogen) in the pulp mill effluents greatly (Young & Akhtar, 1998). However, the use of chlorine dioxide, also give negative impact to the environment by generating chlorate. Chlorate is a powerful herbicide which can severely affect waterborne algae (Stanley, 1996). Hence, TCF bleaching is more preferable to be practiced in the pulp mills in compliance with the environment conservation since the bleaching process is totally free from chlorine compounds (Young & Akhtar, 1998). The TCF usually combines oxygen delignification with peroxide brightening in a series of treatment stages. The chelating agent used in TCF technology is to enhance the bleaching process by forming stable water soluble chelates with the residual of metal ions (Fe, Mn & Cu) in the pulp which should be removed before hydrogen peroxide bleaching. However, the chelation stage may increase the metal load in effluents and impacts the environment considerably (Stanley, 1996).

2.1.1 The abatement of pollution from pulp and paper mill

The modern pulp and paper mills are under constant pressure to have abatement programs within the mills in order to comply with the environment regulations. Thus, the cost of effluent treatment is expected to be included in the budget of the build of new pulp and paper mill. The treatment can be in one stage or two stages depend to the pulp mill's budget and awareness of the environment. Before discharging spent liquor into downstream, the liquor undergoes primary and secondary treatment. After the second treatment, some of the high budget mill also included tertiary treatment (Smook, 1992; Biermann, 1996).

Primary treatment is a removal of suspended solids (85-100 wt. % of solids) from effluent. This treatment is always accompanied by some reduction in BOD and toxicity and further reduced by biological treatment or secondary treatment. Usually two principle methods were employed by the pulp and paper mill which are gravity sedimentation and dissolved-air flotation. Although flotation process is more efficient in removing solids but sedimentation are more commonly used by the pulp mills. Flotation process is expensive to operate whereas the sedimentation only requires little attention and maintenance (Smook, 1992). Ultrafiltrations have also been tried, but have been determined to be futile in removing total dissolved solids completely (Moghe et. al., 2005).

Secondary treatment is a purification process under contained and controlled conditions and in accelerated rates. The treatment is applying nature process by using the microorganisms (bacteria and fungi) under aerobic conditions. The microorganisms consume oxygen to convert organic waste into carbon dioxide and water (Smook, 1992; Lora & Escudero, 2000). The simplest form of aerobic treatment is the oxidation lagoon which can remove up to 85 to 90% BOD. Apart from that, aeration lagoon, activated sludge and biological filter are also widely used in some of the pulp and paper mills to treat the effluent if land is not available or not enough for oxidation lagoon. However, each of this treatment has their own disadvantages. Many mills prefer oxidation lagoon although it required a large piece of land to build the lagoon (Smook, 1992; Biermann, 1996).

Tertiary treatments are advanced treatments after the second treatments. In this stage, the effluent usually undergoes colour removal since primary and secondary treatment could not remove the colour of the effluent totally. The colour of effluent is due to the presence of tannin and lignin derivatives compounds which are slow to biodegrade. External treatments such as lime, alum, polymer coagulation, membrane processes, activated carbon adsorption and filtration through soil substrates (rapid infiltration) are capable providing varying degrees of color removal (Smook, 1992; Biermann, 1996).

Air pollution abatement is more toward to the implementation of guidelines that is related to the design and operation of the recovery boiler system and the collection/ incineration of non-condensible gases and vapors from cooking and evaporation operations (Smook, 1992). In-process air pollution abatement steps are usually aimed at odour reduction since the elimination of odour is impossible. In recent years, most of the pulp mills employ the newer-generation “low-odour recovery boilers” rather than addition of oxidation step which is necessary in mills that still utilize direct-contact evaporator in order to reduce TRS emissions. Furthermore, many mills switch saltcake (Na_2SO_4) to sulfur-free chemicals caustic soda (NaOH) and soda ash (Na_2CO_3) as a soda makeup chemical. Apart from these, evaporator and recovery boiler manufacturers also have improved their designs to achieve higher solids liquor for firing and better mixing within the combustion zone of the furnace (Smook, 1992; Biermann, 1996).

Control equipment also important in order to remove two types of air pollutants, namely particulates and gases/ vapors. The main categories of equipment for removing particulates and gas/ vapor pollutants from effluent gas streams are listed in Table 2.3.

Table 2.3: Air Pollution Control Equipment

Gas/Vapor Removal	Particulate Removal
Catalytic combustion	Mechanical collection
Thermal incineration	Fabric filtration
Adsorption	Gravel bed filtration ("dry scrubbing")
Wet scrubbing	Electronic precipitation Wet scrubbing Hybrid designs

(Smook, 1992)

2.2 Black liquor

Black liquor is an alkaline and complex liquid with high pH (11.5 – 13.5) (AFPA, 2003). The black liquor also has a high biochemical oxygen demand (BOD) with around 13-17 g/l and 40-50 g/l for chemical oxygen demand (COD) due to high lignin, organic and inorganic contents (Furber, 2004; AFPA, 2003). COD and BOD are important parameters for measurement of organic matter content and oxygen needed to decompose the organic compounds. If COD or BOD content of the water is excessive, the oxygen supply in the water may be depleted below the level required to sustain aquatic life (Moghe et. al., 2005). The required COD value to be considered safe is not more than 15 g/l. In addition, black liquor contains high amounts of phenolic compounds, which have a powerful toxic effect on microorganism even at low concentrations (Mishra et. al.,1995; Fortuny et. al., 1998).

2.2.1 The recovery of chemical from black liquor

Normally, in most large and medium scale modern pulp mills, the black liquor was recycled in the plant site and incinerated for chemical recovery and energy. By the installation of conventional chemical recovering system, the pulp mills able to compliance with environmental regulation set by the government standards. Most modern pulp mills concentrate the black liquor by using multiple effect evaporators, followed by incineration, smelting and causticization operations in order to recover the cooking chemicals (Gullichsen & Fogelholm, 2000).

However, this recovery system can only be employed economically for conventional kraft pulping process of hardwoods or softwoods. Hence, it is difficult to employ this process in soda pulp mills particularly non-wood where is used as a raw material (Saroha et. al., 2003). This is mainly due to owing to the non-wood soda pulp mill low capacity and economic constraints. Many of the pulp mills processing non-wood resources cannot afford the capital-intensive system developed for processing much larger quantities of spent liquors, such as those used in wood pulping operations for recovery of energy and recycling of cooking chemicals.

Consequently, many small non-wood mills are forced to discharge their pulping effluents with no treatments into the downstream. Even though, some of the small mills tried to treat the black liquor with secondary biological treatment before discharge to the downstream, but still the rate of pollution is high and also the loss of valuable chemicals (Saroha et. al., 2003).

2.2.2 The recovery system

Chemical recovery is a recovery of chemicals from spent pulping liquor by reconstitutes the inorganic constituent, mostly sodium to form fresh cooking liquor (Smook, 1992). The use of chemical recovery system was not widely practiced until 1930s although the system was available. But, the development of new equipment and an increase in mill size made it more economical to process black liquor than to buy new chemicals. The recovery of black liquor has several advantages. Incineration of concentrated black liquor releases energy to generate steam and electricity as well as able to reduce air and water pollution (Gullichsen & Fogelholm, 2000).

Normally, kraft recovery unit operations consist of:

- Evaporation

  The residual liquor is concentrated in multiple-effect evaporators to form “strong black liquor”. The evaporation process is needed before any recovery could be done to produce black liquor of sufficient high concentration with minimum chemical losses. The fresh weak black liquor obtained from pulping process usually with a solid content between 13-17%. This low concentration black liquor would pose a problem in burning because more heat is required. Therefore, the black liquor must undergo concentration to 60-80% of solids for efficient energy recovery. At this stage, liquor had been concentrated to 50-60% solids, ‘strong liquor’. Then, the liquor need to further concentrated to 65-70% or higher for burning, either by direct-contact evaporation or in a ‘concentrator’.

- Combustion

  The recovery boiler is the main part of the kraft recovery process. Concentrated black liquors contain organic dissolved wood residues and inorganic cooking chemicals. Combustion of the organic portion of liquor in a recovery boiler will form sodium sulfide and sodium carbonate and thus, produce heat. Then, the heat produces high pressure steam to generate electricity and low pressure steam for process use.

- Causticizing

  The causticizing process converts sodium carbonate in green liquor to caustic soda (NaOH) and removes various formed impurities from the boiler and lime kiln. The process begin with dissolving the smelt of recovery boiler in weak liquor to produce green liquor, then remove dregs by filtration or settling and reacts with lime (CaO) to form white liquor.

- Regeneration

The precipitated lime mud ($CaCO_3$) was removed by the white liquor. A lime kiln calcines lime mud ($CACO_3$) to reactive lime (CaO) by drying and subsequent heating (Gullichsen & Fogelholm, 2000; Smook, 1992).

2.2.3 Characteristic of black liquor

Black liquor generated from the pulping process in pulp mills contains water, organic residue from materials and inorganic from cooking chemicals. During the pulping process, about half of the lignocellulosic biomass materials dissolved into black liquor. The dissolved organics consist primarily of lignin and degraded carbohydrates products (hemicellulose and cellulose) while the minor are extractives, proteins and inorganic constituents (Wallberg et al., 2006; Sjostrom, 1992; AFPA, 2003). Typical content of spent liquor from various pulping conditions are listed in Table 2.4. The exact composition of the black liquor varies considerably between different mills depending on the cooking conditions and feedstock (Smook, 1992; AFPA, 2003).

Table 2.4: Typical composition of the kraft, soda and sulfite spent liquor resulting from various pulping condition

	Content (% of dry solid)		
Components	Kraft liquors[a]	Soda liquor[b]	Sulfite liquor[c]
Lignin	39-54	15-35	55*
Degraded carbohydrates	25-35	25-41	28
Extractives	3-5	n.a.	4
Inorganic components	18-25	n.a.	n.a.

* In form of lignosulfonates

[a] (AFPA, 2003; Rojas et. al, 2006)

[b] (Feng et. al, 2001; Feng et. al, 2002; Mohd Ibrahim & Chuah, 2004; Sun et. al, 1999)

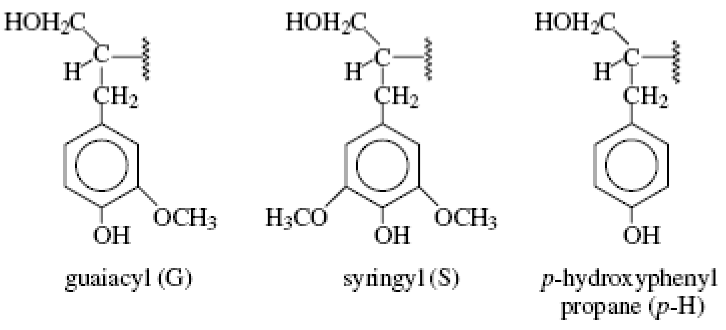
[c] (Sjostrom, 1993)

2.2.3.1 Organic components

Organic components usually degraded from raw materials such as hardwoods, softwoods or non-wood fiber during pulping process into spent liquor. These materials mainly composed of lignin and carbohydrates (cellulose and various hemicelluloses), where the cellulose is embedded in a cross-linked matrix of lignin and hemicelluloses that bind the fibers (Biermann, 1999; Sjostrom, 1993). During pulping, lignin is dissolved into the cooking liquor, resulting in simultaneous fiber separation. In conjuction with delignification, some polysaccharides degradation by-product, including a significant proportion of hemicelluloses and a minor proportion of cellulose are also dissolved or degraded by the alkali-catalyzed cooking reactions (Sjostrom, 1993; Smook, 1992; Casey, 1980).

a) Lignin

Lignin is a phenolic polymer, non-carbohydrate, is created by enzymatic polymerization of three monomers, coniferyl alcohol, synapyl alcohol and *p*-coumaryl alcohol that form to guaicyl (G), syringyl (S) and p-hydroxyphenylpropane (*p*-H)-type units respectively as shown in Figure 2.1. The combinations of these different units form a complex macromolecule with various functional groups and over 10 different types of linkage (Abreu et. al., 1999; Tsujino et. al., 2003). These structures are linked by a multitude of interunit bonds which include several types of ether and carbon-carbon linkages (Mansouri & Salvado, 2006). Lignin generally contains methoxyl groups, phenolic hydroxyl groups and few terminal aldehyde groups. Only a small proportion of the phenolic hydroxyl groups are free since most are occupied in linkages to neighbouring phenylpropane linkages (Ford, 1986; Theander, 1985; Tejado et. al., 2006).



guaiacyl (G) syringyl (S) *p*-hydroxyphenyl propane (*p*-H)

Figure 2.1: Schematic representation of the structural units of lignin (Tejado et. al, 2006)