Abstract—Spent pulping chemicals along with liberated lignin called black liquor are a major liquid waste stream from wood digestion process. For wastewater quality improvement, lignin residue could be isolated via various techniques. According to difference in chemical pulping processes (kraft and soda), variations of organic and inorganic substance were suspended in waste stream. This research aims to investigate the effects of the cooking chemical on organic waste (lignin) in black liquor. Organic waste in black liquor was isolated as soda lignin (SL) from soda black liquor (SBL) and kraft lignin (KL) from kraft black liquor (KBL) by acidic precipitation. In addition, lignin model compound (LMC) was used to establish base case measurement. The elemental analysis revealed the similarity of C, H, and O content of samples in range of 32-33%, 3-4%, and 35-38%, respectively. FTIR results showed that structures of lignin, functional group and guaiacyl to syringyl ratio were vary depended on type of chemical pulping with β-O-4 as the primary composition of the samples. Moreover, Py-GC/MS technique was applied for analyzing the degradation products in order to corroborate the result with the structure and thermal behavior analysis. The TGA results showed high stability of lignin up to around 400°C. Main degraded compounds of all samples were phenol, vanillin, catechol, and guaiacol. This finding suggested that not only lignin which caused high BOD and COD could potentially be isolated for value added product but also the discharge quality could be improved. In addition, different chemical processes effect residual lignin in black liquor and underscore the importance of lignin in black liquor as a potential material for renewable energy and chemical production.

Index Terms—Pulp and paper wastewater, black liquor, lignin, elemental analysis, FTIR, TGA, Py-GC/MS.

I. INTRODUCTION

The important necessity for human living and environmental balance is water controlled by natural influences e.g. geological, hydrological and climatic. However, the anthropogenic activities have influenced the water quality [1], [2], especially the surface waters which are threatened with the pollution from domestic, agricultural, and industrial wastes. River, although, is the essential water resource for any creature existing, discharges from their processes have been released into the natural water bodies. Therefore, the effluent must be controlled, in particularly, industrial wastewater because of its various contaminants.

As the global competition and society pressure, emission reduction management, especially the industry sector, are the requirement for sustainable development. [3] In Thailand, zero discharge is the measurement for industrial wastewater management to enforce the factory drainage quality. The treated wastewater met the standard requirement are lawful release, nevertheless, there are difficulty to limit the amount due to the specific process of each industrial type, e.g. pulp and paper industry. According to Department of Industrial work in 2015, there are 103 pulp and paper factories in 29 provinces through five regions in Thailand, almost the half are in the central part of Thailand.

Pulp and paper industry consume the intensive water for chemical process led to the enormous quantities of wastewater around 20 to 250 m³ per ton of pulp yield. [4] Lignin in raw material is by-product from the pulping process mixed in the spent chemical solutions that called black liquor containing a variety of organic and inorganic contaminants. [5] Due to high calorific value, lignin would be burnt as fuel in the recovery boiler even though many problems come with this method, e.g. smelt-water explosions, corrosion, and plugging. [6] Moreover, low efficiency evaporation of salt recovery process causes the organic pollutant from salt impurity. [7] As a result, this wastewater contains high biochemical oxygen demand (BOD), chemical oxygen demand (COD) due to the pollutants from production process i.e. alkali–lignin and polysaccharide degradation residues. [8], [9] Furthermore, their dark coloration have negative impact on aquatic fauna and flora [10] since lignin and its derivatives. [11] Thus the strict environmental regulations for pulp and paper industry are enforced, resulting in various technologies to improve discharge quality by elimination of lignin.[12]

Naturally, lignin composed of difference functional groups and aromatic base structure. [13] Various value added products could be produced from lignin, such as biomedical materials, copolymer composites, resins, antioxidants, adsorbent, catalysts and catalyst support and carbon electrodes. [14], [15] Moreover, lignin utilization as the biomaterial for any productions that normally derives form petrochemical based has driven as its potential and environmentally friendly material required. Varieties of lignocellulosic material utilization, organic waste has continuously generated especially for lignin substance. [16] There are two major pulp and paper manufacturers in Thailand which use the same wood (eucalyptus) but different chemical pulping processes. Kraft and soda pulping processes are the major alkali digestion in paper making mills. After wood chopping, wood chip was boiled with cooking
chemical in the digester tank. Sodium hydroxide (NaOH) and sodium hydroxide with sodium sulfide (Na₂S) are the principal cooking chemicals for soda and kraft process. Cooking chemical functions as the separating tool to divide lignin from fiber which is further paper production. The divided lignin and the spent chemical are drained together as black liquor. [17]

However, the chemical in the digestion process might effect the structure of lignin in waste stream from pulping process. Therefore, this research aims to isolate lignin from black liquor for lignin powder and then investigate the effects of cooking chemical in alkali puling to lignin residues. Several characterization techniques were used to reveal the properties in term of thermal behavior and functional group in samples. Industrial black liquor from kraft and soda process was studied as the initial substance of extracted lignin. Lignin model compound was used as the comparable in properties to other samples.

II. METHODOLOGY

This study focused on industrial black liquor and extracted lignin isolated from these samples. Lignin model compound was used as the comparable sample in extracted lignin. Many characterization techniques were used to determine the properties of samples.

A. Samples

Weak black liquor samples were obtained from local paper making industries consumed Eucalyptus tree as the raw material. Kraft black liquor (KBL) and soda black liquor (SBL) from kraft pulping and soda pulping, respectively were performed at different pH (12 and 9 for KBL and SBL) and %solid (15 and 13 for KBL and SBL). They were collected at the position of after the alkali digestion and before evaporation unit. Extracted lignin was obtained from acid precipitation (H₂SO₄) of weak black liquor. Lignin model compound was purchased from Sigma-Aldrich for being the precursor of lignin characterization.

B. Lignin Precipitation

Lignin in weak black liquor was precipitated (adapted from Hu et al, 2013 [17]) by pH adjusting at room temperature with 50%wt H₂SO₄ until reaching pH 2, and then further stirring for 1 hr. The acidified black liquor was washed by DI water until the washed water was neutral. After gaining the neutral washed water, the remaining solid in a lower layer was dried again at 60°C for 12 hours. The extracted lignin from KBL was kraft lignin (KL) whereas from SBL was soda lignin (SL).

C. Thermal Properties Analyses

The properties of all samples were shown in Table I. The American Society for Testing and Material was used for classifying the sample as of moisture (ASTM E871, 2006), volatile matter and fixed carbon (ASTM E872, 2006), and ash content (ASTM D1102, 2007) for the proximate analysis. The carbon, hydrogen, nitrogen, sulfur and oxygen contents of samples were determined for ultimate analysis using Leco TruSpec® CHNS (micro) analyzer in weight percentage. In addition, the lignin composition of black liquor was determined by TAPPI-T222-om-98 in dried weight percentage. Bomb calorimeter (Leco model AS–350) with ASTM D240 (2009) was used for the higher heating value of black liquor. Metter Toledo, TGA/SDTA 851® was employed to investigate the mass loss of samples. Samples of about 3-5 mg was placed and heated from 30 - 800°C in the oven at 20°C/min heating rate and 60 mL/min flow rate of nitrogen gas to maintain the inert atmosphere.

D. X – Ray Fluorescence

Inorganic components were investigated using the Philips, PW–2404, 4kW (wavelength dispersion). The concentration of compound was determined in weight percentage.

E. X – Ray Diffraction

The crystallinity of black liquor, extracted lignin and lignin model compound were studied by X’Pert Pro MPD diffract meter with a Cu Ka radiation which was operated at 40 kV and 40 mA.

F. FTIR Analysis

FTIR spectra of black liquor and extracted lignin were recorded on the FTIR Spectrometer (Perkin Elmer System 2000). The KBr pellet was using with 1% samples. The scan was conducted in the range of 4000 cm⁻¹ to 600 cm⁻¹.

G. Py – GC/MS

Fast pyrolysis experiments were carried out at 500°C for 0.5 min in a pyroprobe which is the multi–functional pyrolyzer (PY-202iD, Frontier Lab). The reactions worked with the auto–shot sampler AS–1020E interfaced to a gas chromatograph couples to a mass selective detector (GC/MS – QP2010, Shimadzu) for separating and identifying the products. Extracted lignin and lignin model compound were contained in the sample cup, plugged by quartz wool, and inserted into the heat zone for 0.5 min. The samples were pyrolyzed at the same temperature and reaction time in helium atmosphere. The volatile products from the reaction were achieved on an ultra–alloy capillary (UA5–30M–0.25F, 30m × 0.25mm × 0.25 μm film thickness). The spit injector ratio was 1:50 with 1.1 mL/min gas flow rate of carrier gas. The GC oven was begun at 50°C held on 3 min and reached to 200°C at the heating rate of 5°C/min, and then reached at 350°C with 10°C/min 10 min holding time. The temperature holding of injector and detector was 280°C. The mass selective detector was performed as the analyzer of the volatile compounds in electron impact mode at 70 eV over the range from mass ion (m/z) of 20 – 800. The spectra identifying was carried out by the matching the mass ion of each peak with the NIST mass spectral library.

III. RESULTS AND DISCUSSION

A. Elemental and Thermal Analysis

Thermal characterization results of KBL, SBL and LMC are displayed in the Table I. High water content as 80% clearly illustrated the pulping process which generates weak black liquor. Kraft and soda black liquors were slightly equal amount of carbon element.

Thermal characterization results of KBL, SBL and LMC are shown in the Table I. Because they are weak black liquor from the alkali digestion tank, KBL and SBL composed of
high water content as 80%. Carbon and oxygen components were the major element of black liquor. However, KBL was from Kraft process which consumes Na₂S and NaOH as the alkali chemical, led to higher sulfur content of KBL than SBL. Lower heating value and lignin composition of KBL was higher than SBL about 7% and 14%, respectively.

### Table I. Proximate, Ultimate, Heating Value and Lignin Composition Analysis of Industrial Black Liquor

| Analysis method                  | Element (wt%) | Value | KBL   | SBL   |
|----------------------------------|---------------|-------|-------|-------|
| Proximate analysis (TGA)         | Moisture      | 80.2  | 81.4  |
|                                  | Volatile matter| 11.3  | 11.0  |
|                                  | Fixed carbon  | 0.4   | 0.4   |
|                                  | Ash           | 7.2   | 5.2   |
| Ultimate analysis (CHNS/O)       | C             | 33.0  | 32.8  |
|                                  | H             | 3.4   | 4.2   |
|                                  | N             | 0.1   | 0.2   |
|                                  | S             | 5.1   | 0.3   |
|                                  | O             | 35.3  | 38.7  |
| Low heating value (Bomb calorimeter) | LHV (MJ/kg) |       | 12.3  | 11.4  |
| Lignin composition (TAPPI-T222-om-98) | Lignin (dw%) |       | 27.8  | 24.0  |

Elemental and TGA analysis results were together revealed the effects of ash content in black liquor. From the TGA graphs of KBL, SBL, KL, and SL (in the TGA analysis results part) were unambiguously showed an increased solid residue of extracted lignin compared to black liquor. Because inorganic could not be completely degraded by heat, higher solid content was remained. Therefore, solid residue of KBL was relatively larger than SBL conformed to the wt% of ash in Table I. Moreover, inorganic content could not be appreciably degraded by thermal degradation, lignin isolated from black liquor had lower solid residue comparing with the initial black liquor before precipitation. Because lignin is organic part in black liquor, after acid precipitation, the inorganic remained with the spent acid solution. Lignin, therefore, was easier to be removed than black liquor, leaving less amount of solid residue.

### B. Wastewater Treatment by Organic Lignin Removal

Lignin yields isolated from weak black liquor were 27% and 24% of KBL and SBL, respectively. Color of extracted lignin was dissimilar. Lignin from KBL was black while dark brown in SBL yield. Wastewater improvement by this method would be reported on COD and BOD₅ estimated from %organic lignin. Characteristic analysis results revealed the chemical structure of extracted lignin compared with the commercial lignin (lignin model compound) for further utilization as biomaterials.

Organic content in wastewater was removed and turned into lignin product, instead to the pollutant for wastewater treatment plant. COD and BOD₅ can be indirect estimated by %organic matter. Initial lignin contents in wastewater of KBL and SBL were converted into initial COD and BOD₅, whereas removal COD and BOD₅ were calculated by % lignin extraction. The first step to estimate, %lignin were conversion to total organic carbon (TOC) due to obvious correlation between lignin and soil. [18] To estimate %TOC, lignin percentage in waste stream was calculated by the factor of 1.72 [19] as the equation (1).

\[
\%\text{organic matter} = \%\text{TOC} \times 1.72 \tag{1}
\]

TOC in mg/L was used to estimate for COD and BOD as equations (2) and (3) [20] and results were in Table II.

\[
\text{COD (mg/L)} = 49.2 + 3.0\text{TOC} \tag{2}
\]

\[
\text{BOD₅ (mg/L)} = 23.7 + 1.68\text{TOC} \tag{3}
\]

The efficiency of organic waste removal from kraft and soda wastewater by lignin extraction was more than 95%.

### Table II: COD and BOD estimation by %lignin content

| Waste steam          | Parameter     | KBL   | SBL   |
|----------------------|---------------|-------|-------|
|                      | % initial lignin| 27.8  | 24.0  |
|                      | %TOC           | 16.2  | 14.0  |
|                      | TOC (mg/L)     | 161.6 | 139.5 |
|                      | COD (mg/L)     | 534.1 | 467.8 |
|                      | BOD₅ (mg/L)    | 295.2 | 258.1 |
| Lignin extraction    | % lignin       | 27.0  | 23.0  |
|                      | %TOC           | 15.7  | 13.4  |
|                      | TOC (mg/L)     | 157.0 | 133.7 |
|                      | COD (mg/L)     | 520.2 | 450.4 |
|                      | BOD₅ (mg/L)    | 287.5 | 248.3 |

### C. Chemical Structure Characteristic

1) X-ray fluorescence characteristic

To investigate the inorganic component of industrial black liquor from kraft and soda process, the sample was analyzed and shown as the percentages of K, Cl, Ca, and Fe in Table III.

### Table III: XRF results of industrial black liquor, KBL and SBL

| Industrial black liquor | Elements (wt%) | K     | Cl    | Ca    | Fe    |
|------------------------|----------------|-------|-------|-------|-------|
| KBL                    |                | 3.86  | 1.12  | 0.15  | 0.01  |
| SBL                    |                | 2.60  | 0.88  | 0.11  | 0.01  |

The content of potassium, chlorine, and calcium of KBL was higher than SBL. This conformed to the ash content in the proximate analysis (Table I); ash of KBL was larger than SBL 27.8%. However, the ferrous content could indicate the corrosion inside the digestion reactor, clearly illustrated in Fig. 1. The XRD of black liquor (Fig. 1) showed that the CaFe₅O₇ compound in SBL was higher than KBL which could be confirmed from 50% Fe content in SBL higher than KBL (Table III).

2) X-ray diffraction

![Fig. 1. XRD pattern of industrial black liquor from kraft pulping (KBL) and soda pulping (SBL).](image_url)
The crystallinity of inorganic compounds in KBL and SBL are shown in the Fig. 1. The principal compound of SBL was sodium carbonate (Na₂CO₃) according to JCPDS: 18-1208, at the 2θ of 30°, 35°, and 38° were the located main peaks.

Due to the initial chemical substrate in the pulping process, Na₂SO₄ was in the major compound of KBL, whereas Na₂CO₃ was main component of SBL, according to JCPDS: 37-1465. [21] However, peaks of SBL was sharper than KBL, it could be the larger NaCl (JCPDS: 99-0059) in SBL. Moreover, CaFe₃O₄ was found in both of industrial black liquor according to the JCPDS: 39-1033. Nevertheless, after lignin isolation process, the inorganic contents in black liquor were eliminated; the amorphous of extracted lignin was shown in the Fig. 2.

![Fig. 2. XRD pattern of extracted lignin from industrial black liquor (KL and SL) and lignin model compound (LMC).](image)

The amorphous phase of extracted lignin, KL and SL, were similar to LMC which could indicate the potential of black liquor as the innovative material for renewable energy resource. However, disappear of salt peak on KL and SL compared to the pattern of black liquor might be the evidence of the difference results due to dissimilar precipitation procedure. Santos et al. [21] isolated lignin using the method of Alriols et al. [22] who twice washed lignin after sulfuric acid precipitation. Lignin extracted using this method showed Na₂SO₄ salt peak as described in JCPDS 37-1465, and NaCl (JCPDS 5-0628) salt peak in case of hydrochloric precipitation. This research precipitated lignin using Lu et al. [23] method which suggested washing acidic lignin by distilled water until the washed water was neutral. From Fig. 2., extracted lignin performed the purity as the LMC.

3) FTIR analysis

FTIR spectra of KBL, SBL, LMC, KL, and SL were displayed in Fig. 3. Bands were assigned according to Silverstein et al. (1981) [24], Shen et al. (2010) [25], and Yuan et al. (2011). [26] Black liquor and extracted lignin showed similar spectrum with variant on some peaks. All of samples showed a broad band centered at 3400 cm⁻¹, attributed to the O – H stretching vibration in the phenolic and aliphatic structures. Comparing KBL and SBL with LMC, the structure of industrial black liquor was similar to commercial lignin, suggesting the potential of waste stream from pulping process as raw material for lignin compound production. The bands around 2900 cm⁻¹ and 2850 cm⁻¹ of KL and SL was sharper than in KBL and SBL, might suggest the effects of acid precipitation. The symmetrical and asymmetrical C – H stretching in methyl and methylene group could be found at 2900 cm⁻¹ and 2850 cm⁻¹, respectively. Therefore, higher aliphatic structure appeared in the extracted lignin due to abundance of fragmented lignin structure after acidified isolated.

![Fig. 3. FTIR spectroscopy spectra of industrial black liquors, extracted lignins, and lignin model compound.](image)

Bands were assigned around 1600 cm⁻¹ – 600 cm⁻¹ represented the identity of any substance. Carbonate salt performance can be found at around 1429 cm⁻¹, 880 cm⁻¹ and 694 cm⁻¹ of SBL, whereas at 1587 cm⁻¹, 1416 cm⁻¹, and 1117 cm⁻¹ of KBL showed the pattern of carboxylic salts. However, there were some metal ions on both of black liquor which can be revealed by the XRD result. Industrial black liquor contained sodium compound as the principal metal ion since the chemical in digestion process. Therefore, FTIR band of carboxylic and carbonyl of KBL and SBL were impure. LMC was used for comparable study with extracted lignin, however, FTIR result revealed some impure in LMC structure. Moreover, KL showed accuracy pattern of standard lignin model compound instead of LMC, while the identity of cellulose pattern could be found on spectrum on SL. Therefore, the black liquor from different process might produce the different lignin content in waste steam and led to dissimilar structure of organic content in black liquor. The differences of chemical structure in samples might be the reason of diverse results in thermal reaction behavior; further discussion was in next part.

D. Thermal Degradation Results

1) TGA analysis

Thermal behavior analysis of lignins was used to study kinetics of reaction at various temperatures. The first losing stage (80-200°C) was the evaporation of moisture and some volatile organics [27] appearing with all samples (Figs. 4 and 5). The temperatures at which the black liquor begins to degrade are around 200°C, similar for all three lignins. There were clearly three steps for degradation of black liquor not including water evaporation whereas only two steps for all lignin samples. The different weight loss steps might be revealed some various mixtures of substances in all samples. The highest degradation temperature was in range of 200-400°C as 19.7% and 20.6% for KBL and SBL, respectively which suggested the loss of hemicellulose and cellulose contents. [28]
Due to high thermal stability, lignin was the content which difficult to degrade and had a wide range of decomposition temperature. Therefore, the remaining mass was almost from lignin which KBL had the greatest amount as 58.8% remaining since the kraft pulping process can effectively separate lignin from wood and drain along with spent chemical forming as black liquor. Moreover, the remaining percentages of samples were very high (> 40wt.%), suggesting that the predominate as lignin was the main part of all feedstock. [28]

2)Py – GC/MS

In order to investigate the potential of extracted lignin for further utilizing as raw material in place of those that normally derived from petrochemical based. Pyrolysis reaction of extracted lignin, KL and SL, and LMC were carried out at 500°C for 0.5 min. The results revealed many degraded compounds as shown in Fig. 6.

Aromatic compounds were primary products for all samples; however, KL yielded the highest variety of phenolic compounds. From the FTIR results, KL was lignin compound whereas SL was cellulose compound. Phenolic compound was major in degraded yield of KL, presented and confirm the lignin properties of KL. Both of KL and SL had favorable potential as raw material in biorefinery for biomaterial and biofuel productions. Especially for valuable chemical, such as adhesives, polymer material, activated carbon, carbon fiber, etc., KL was the suitable feedstock; due to its aromatic base structure. As the feedstock for biofuel via thermal conversion, SL which was similar to cellulose was suitable for thermal cracking reaction. Therefore, the pulping process effected lignin structure in black liquor and could enhance the appropriate method for high efficiency utilization in the future.

IV. CONCLUSION

Black liquor from pulping industries has a potential for being the lignin source for production of fuel and chemicals normally derived from petroleum-based process. Lignin residual isolation not only can recover bio-material from wastewater, but also can improve wastewater quality through organic waste mitigation. The characteristic results showed the different properties of black liquor from kraft (KBL) and soda processes (SBL). The main organic compounds of KBL and SBL were carboxylic salt and carbonate salt, respectively. Predominant inorganic element was sodium originated from the cooking chemical in the digester tank, NaOH. However, inorganic compound which may lead to corrosion was found in KBL, suggesting the effect of Na₂S on the material of tank in the kraft process. Moreover, the extracted lignin from the industrial black liquor had the dissimilar structure which might be affected by the pulping process. FTIR results revealed that the structure of KL was the similar to pure lignin model compound, whereas SL was same as cellulose.
model compound. In addition, KL pyrolysis produced a complex and variety of aromatic compounds, while some cellulose derived products were found in SL pyrolysis. However, because of their chemical compositions, lignin which was isolating from the industrial steam waste of pulping process has a potential for being raw material for renewable energy and valuable chemical productions.

**CONFLICT OF INTEREST**

The authors declare no conflict of interest.

**AUTHOR CONTRIBUTIONS**

A. Duangduen and S. Viboon helped supervise the project; H. Yotwadee performed the experiments and drafted the manuscript with great support from A. Duangduen and S. Viboon; all authors had approved the final version.

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