Pyrolysis of hardwood soda-anthraquinone spent pulping liquor

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ABSTRACT: A lignin-rich feedstock, soda-anthraquinone spent pulping liquor, was pyrolyzed in a kiln reactor. The liquor was prepared from mixed northern hardwood chips at a liquor-to-wood ratio of 3.5 L/kg, 16% effective alkali, and an *H*-factor of 1000 h. The spent liquor was pyrolyzed at 500°C as is, after oxygen oxidation, and with addition of sodium formate to determine the effect on bio-oil yield and product distribution. Contrary to bio-oil from sawdust, a clear phase separation of the liquid product into an aqueous layer and a denser organic layer is obtained. The predominant products found in the organic layer collected after pyrolysis are phenols with varying degrees of methylation and ethylation. The organic yield appears to go through a maximum (32 wt% on spent liquor organics) at around 25 wt% formate added on spent liquor dry solids and subsequently decreases at greater charges. Oxidation of the spent liquor prior to pyrolysis appears to have a detrimental effect on the organic yield.

Application: This study demonstrated that significantly deoxygenated, value-added liquid organics can be produced from spent pulping liquor using a robust processing technique at atmospheric pressure, while the solid product remaining after processing can be recycled in a kraft recovery cycle to regenerate pulping chemicals.

The desire to replace petroleum-based chemicals by those produced using renewable feedstocks has gained much interest recently. In particular, chemicals produced from lignocellulosic resources have become an attractive alternative due to the renewable nature of the feedstock and its ability to fix carbon dioxide (CO_2) during its growth period [1,2]. Of the three main components in lignocellulosic biomass, lignin is an attractive starting material due to its abundance as the largest natural aromatic polymer on earth, nominal usage beside combustion, and significant production predicted in the lignocellulosic biorefinery [3]. Phenols are of particular importance as they serve as building blocks for many commercial products, including polycarbonates and phenolic resins currently derived from petroleum-based resources [4]. Various chemical pulping processes (i.e., kraft, soda-anthraquinone (AQ), sulfite, and organosolv) produce a lignin-rich byproduct stream known as spent liquor, or black liquor. Aryl ether linkages, accounting for more than 50% of all linkages present in lignin, are cleaved during kraft and soda-AQ pulping, resulting in lower-molecular weight lignin fragments that dissolve in strongly alkaline pulping liquor [5-7]. As a result of peeling reactions during the pulping process, polysaccharides, primarily hemicelluloses, end up in the spent liquor mainly as hydroxy acids [8]. Extractives and pulping chemicals also remain in the spent liquor. Due to the considerable organic content of the spent liquor (approximately 60 wt% of total dry solids) and its large global production of approximately 200 million metric tons of dry solids/year, it has been considered a potential feedstock for the production of value-added chemicals and/or liquid fuels for almost a century [9,10]. Robust lignin valorization processes continue to elude development, however, due to its complex chemical composition, its tendency to form a carbon-rich char upon thermal treatment, and various feeding and processing issues when trying to implement a continuous system [11,12].

In the early part of the 20th century, E.L. Rinman patented a process that utilized spent pulping liquors from sulfate and soda pulping processes to produce a bio-oil that was rich in hydrocarbons, aldehydes, ketones, phenols, and alcohols [13]. The process, known as dry distillation, utilized spent liquor solids that had been thoroughly mixed with sodium and calcium hydroxides prior to evaporation and were subsequently thermally decomposed in the presence of superheated steam [14]. The process operated industrially at a German straw soda pulp mill in Bavaria, Germany, from 1922 to 1929, producing 60-70 kg of low-molecular weight organic compounds per metric ton of pulp produced [15]. While fast pyrolysis of spent pulping liquors has been investigated [16-18], the interest has focused on acquiring an improved understanding of the pyrolysis or devolatilization process of spent liquor droplets during combustion in the recovery boiler and not for the production of value-added products. Most of the recent interest in spent pulping liquors has been focused on gasification [19-21] and high-pressure thermal treatment [22-24].

More recently, fast pyrolysis of lignins has been investigated as a means to produce bio-oils [12,25,26]. Mukkamala et al. demonstrated that the quality of bio-oil produced from fast pyrolysis of Indulin AT (low-sodium lignin isolated from kraft spent liquor) could be improved with the addition of calcium

formate ($Ca(OOCH)_2$) [26]. They demonstrated that with a formic acid-to-lignin mass ratio of 1:1, the bio-oil yield increased to 32.5 wt% from 23.3 wt% for Indulin AT mixed with calcium hydroxide ($Ca(OH)_2$) only. The char yield, oxygen-to-carbon ratio, and higher heating value were also improved. It is well known that at elevated temperatures, $Ca(OOCH)_2$ decomposes into calcium carbonate ($CaCO_3$), carbon monoxide (CO), and hydrogen (H_2), thus providing an *in situ* source of reactive hydrogen to aid in deoxygenation [27]. If liquid transportation fuels are the desired product from thermochemical conversion of lignocellulosic biomass, it is crucial to drastically reduce the oxygen content of the bio-oil derived from this feedstock. This partially deoxygenated and more stable "crude" product requires less upgrading prior to distillation to isolate the different fuel fractions.

Oxidation is a technique that is used to effectively achieve lignin depolymerization. In the pulping industry, the pulp that is separated from the spent liquor after cooking, also called brownstock, is further delignified by oxygen treatment under alkaline conditions to remove about 50 wt% of the residual lignin [28]. The generated oxygen-delignified spent liquor is combined with the spent pulping liquor for chemical and energy recovery. It is known that upon oxygen delignification in the presence of sodium hydroxide (NaOH), the phenolate structures undergo degradation into lower-molecular weight compounds, resulting in an increase in the amount of carboxylic acids formed via ring-opening mechanisms and reactions of the aliphatic side-chain [29-31]. It has been shown that neutralized carboxylic acids are a potential feedstock for the production of bio-oils when combined with formate [32].

In the present study, spent liquor isolated from soda-AQ pulping of mixed northeastern hardwood chips was pyrolyzed at 500°C. The effect of adding sodium formate (0-50 wt% on spent liquor solids) was investigated. Sodium formate (HCOONa) is known to decompose at elevated temperatures similar to the decomposition of $Ca(OOCH)_2$, yielding sodium carbonate (Na_2CO_3), CO, and H_2 [33]. Oxidation with oxygen (O_2) of the spent liquor prior to pyrolysis (with 0-10 wt% NaOH supplementation on spent liquor solids at 145 psig O_2) was also investigated to determine the effect of lignin aromatic ring opening on the bio-oil yield and product distribution. Another motivation for producing value-added products from pyrolysis of spent liquor rather than pyrolysis of lignin that has been precipitated from spent liquors, such as done in the LignoBoost process [34], is that it minimizes processing steps prior to thermal treatment and utilizes all of the organic material that is available in spent liquor instead of only the lignin fraction.

MATERIALS AND METHODS

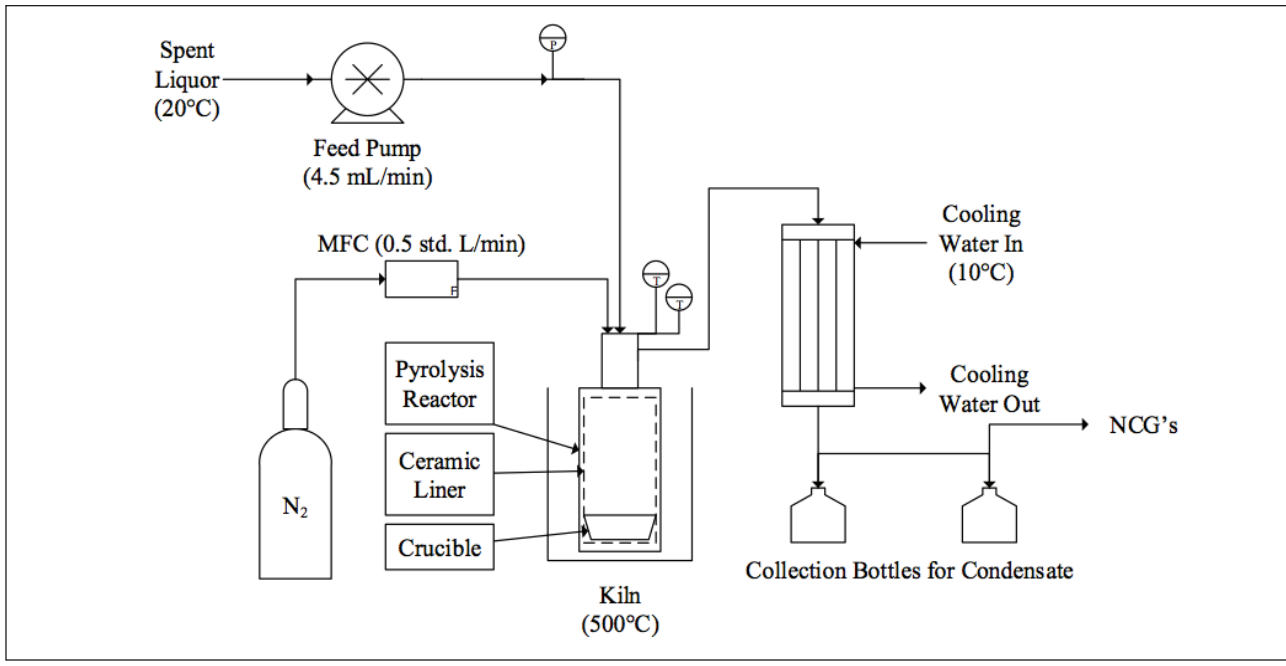
Mixed northeastern hardwood chips were obtained from Old Town Fuel & Fiber (Old Town, ME, USA) and screened. Chips passing through a 9/8 in. screen and collected on a 5/8 in. screen were used for laboratory pulping. All chemicals used in this work were reagent grade.

Soda-AQ cooks

The chips were cooked in a 11.4 L custom-made rocking digester to a target H-factor of 1000 h [35] using the following conditions: liquor-to-wood ratio of 3.5 L/kg, 16% effective alkali as sodium oxide (Na_2O), 3% Na_2CO_3, 0.1% AQ, 160°C, and a steady-state pressure of 80 psig. Three to 4 kg of green chips were used for each cook, yielding 4-6 kg of spent liquor. Four cooks were performed. Following each cook, pulp yield and kappa number (TAPPI Standard Method T 236 om-06 "Kappa number of pulp") were determined. The weak spent liquor was analyzed to determine dry solids (TAPPI Standard Method T 650 om-05 "Solids content of black liquor"), residual effective alkali (REA; modified SCAN-N 33:94 "Residual alkali [Hydroxide ion content]"), and lignin, sugar, and acid content via double acid hydrolysis (modified NREL/TP-510-42618 "Determination of structural carbohydrates and lignin in biomass"). The hydrolysate collected after double acid hydrolysis was analyzed using a Shimadzu Prominence high-performance liquid chromatography (HPLC) system (Shimadzu; Kyoto, Japan) equipped with a refractive index detector and an ultraviolet (UV) detector set at 205 and 280 nm (column: HPX-87H; mobile phase: 5*m*M H_2SO_4; flow rate: 0.6 mL/min; column temperature: 60°C). Acid-soluble lignin was determined using a Nicolet Evolution 100 UV/Vis spectrophotometer (Thermo Electron Corporation; Waltham, MA, USA) (wavelength: 205 nm; acceptable absorbance range: 0.2 – 0.7 A; absorptivity constant: 110 L/g·cm). Klason lignin was determined gravimetrically by drying the filter cake collected after filtration of the hydrolysate in an oven at 105°C until a constant weight was reached. Decomposition temperature ranges and a first estimate of volatiles and non-condensable gases (NCGs) yield were determined using a TA Instruments Q500 (TA Instruments; New Castle, DE, USA) thermogravimetric analyzer (TGA) equipped with an evolved gas analyzer (EGA) furnace (purge gas: N_2; flow rate: 100 mL/min; program: hold isothermal at 20°C for 20 min., ramp at 10°C/min to 700°C; sample size: 10 – 20 mg; pans used: platinum).

Oxidation

Oxidation of weak spent liquor (approximately 1 L) was performed in a 2 L Hastelloy C Parr reactor (Parr Instrument Co.; Moline, IL, USA) operating in batch mode. The reactor was purged in triplicate with pure O_2 (30 psig) prior to heating to 127°C. Once the temperature stabilized, the reactor was pressurized with 145 psig O_2 and subsequently sealed for the 30 min reaction time. Once the reaction was complete, the oxidized spent liquor was cooled rapidly to 50°C and collected. Oxidation was performed on the weak spent liquor as is and on the weak spent liquor with 10 wt% NaOH supplementation on spent liquor solids. Approximately 75 psig O_2 was consumed during the course of the reaction, calculated using the van der Waals equation of state, corresponding to 2.5 wt% and 3 wt% on spent liquor solids for 0 wt% and 10 wt% NaOH supplementation, respectively. These reaction parameters



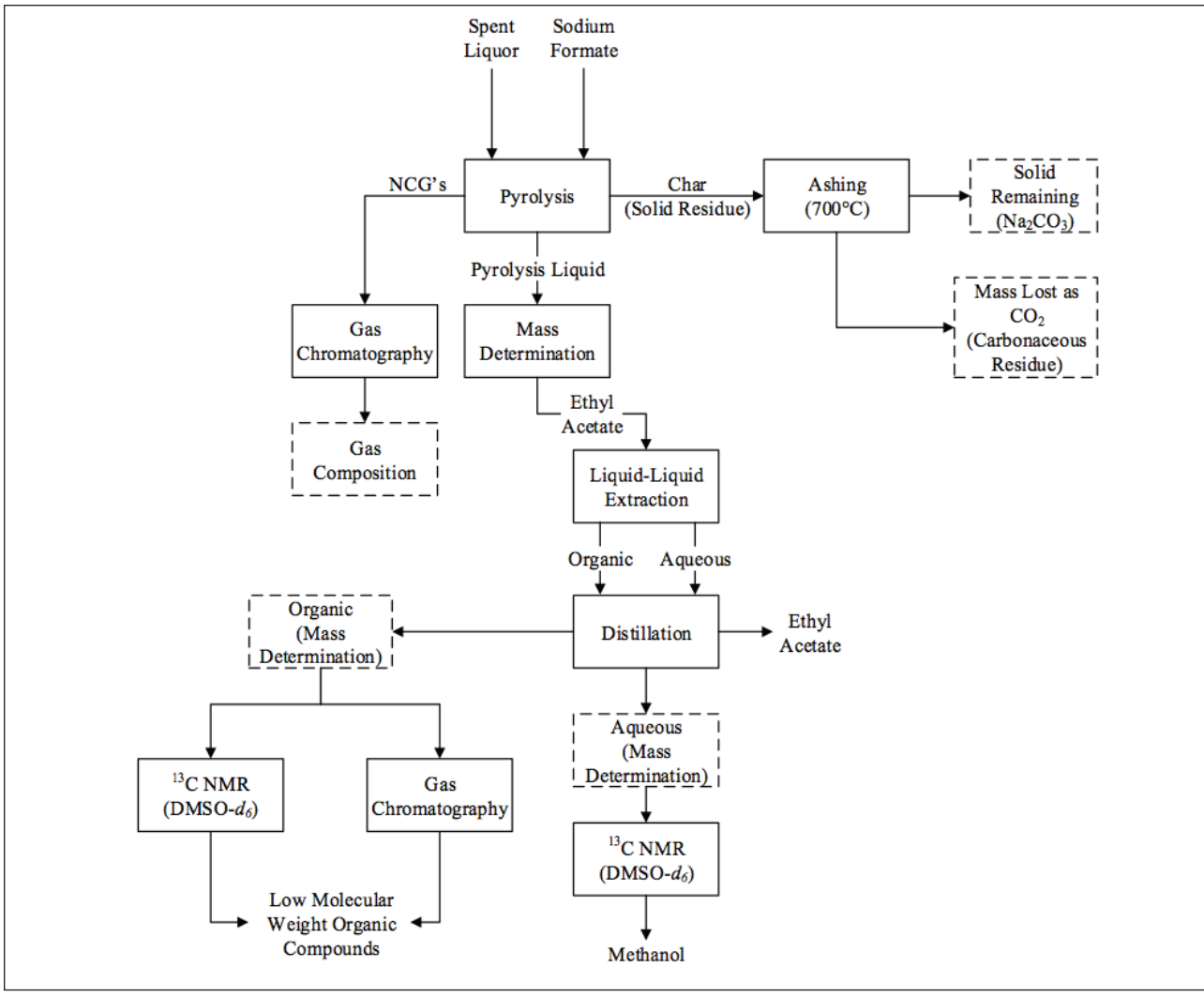
1. Schematic depicting pyrolysis setup.

were determined based on previous unpublished work. The oxidized spent liquor was only analyzed for dry solids content as described earlier.

Pyrolysis

The weak spent liquor was fed to a custom-made kiln reactor at a rate of 4.5 mL/min. Weak spent liquor as is, oxidized spent liquor, and weak spent liquor with 0-50 wt% HCOONa addition based on spent liquor solids were the feedstocks investigated in this work. Nitrogen (N_2) was used to sustain an inert environment and was maintained using a mass flow controller (MFC) flow programmed at 0.5 std. L N_2/min. A schematic of the setup is seen in **Fig. 1**. The feed enters the top of the reactor where each droplet is heated in flight at ambient pressure. The collected hot spent liquor droplets pyrolyze to a char at the bottom of the reactor, while simultaneously liberating volatile products and NCGs that flow through the condenser at the top of the reactor and are collected for subsequent analysis. In this work, char is defined as the carbonaceous residue that forms during pyrolysis plus Na_2CO_3 originating from thermal decomposition of lignin/hemicellulose-derived salts, NaOH, or HCOONa. Feeding times varied from 3-4 h, depending on the amount of feedstock used (approximately 1 L spent liquor). The reactor temperature was maintained at 500°C. Gas samples were analyzed every 30 min beginning 60 min after feeding had commenced to ensure the system had reached steady-state. They were sampled from the gas line leaving the second collection bottle (Fig. 1). An SRI 8610C gas chromatograph (GC, SRI Instruments; Torrance, CA, USA) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) was used to analyze the NCGs and low-boiling compounds that did not condense at the temperature of the cooling water (10°C). Supelco calibration gases were used to determine the volume fraction of each gas of interest. The N_2 content as determined from the GC and the known flow rate of N_2 into the reactor were used to quantify the NCGs and low-boiling compounds produced upon pyrolysis.

The liquid samples collected after pyrolysis were weighed and extracted with ethyl acetate (EtOAc). This was done to neatly separate the viscous and distributed oily layer from the aqueous layer. EtOAc was distilled off from each layer under vacuum using rotary evaporation, and final weights were recorded for mass balance determination. A flow diagram depicting the experimental and analytical procedures used can be seen in **Fig. 2**. After removal of EtOAc by distillation from both the aqueous and organic layers, the organic fraction was analyzed using a Shimadzu GC/MS-QP2010S (column dimensions: 30 m x 0.25 mm x 0.25 µm; carrier gas: He; flow rate: 1 mL/min; injector temperature: 250°C; column temperature: 40°C; column pressure: 49.5 kPa; program: 40°C [hold 1 min], ramp to 120°C at 2°C/min [hold 2 min], ramp to 160°C at 1.5°C/min [hold 2 min], ramp to 250°C at 25°C/min [hold 10 min]). The compounds in the organic layer observed by gas chromatography-mass spectrometry (GC/MS) were compared with a NIST library. Any peaks less than 85% compatible with the known retention time and mass spectra of the identified compound were discarded and remaining peak areas were normalized to 100% to yield semi-quantitative results. The organic layer and aqueous layer were also analyzed using a Varian Unity 9.4 T instrument (Varian; Palo Alto, CA, USA) for carbon-13 nuclear magnetic resonance (^{13}C NMR). Samples were prepared using a 0.3:1 mass ratio of organic:solvent with dimethyl sulfoxide-d_6 (DMSO-d_6) as the solvent. ^{13}C NMR spectra were acquired with an 84° pulse angle, a 4.5 s pulse delay, a sweep width of 25,000 Hz, and full proton



2. Experimental design depicting methods by which mass balance closure was obtained, as well as analytical techniques utilized for product characterization. Dashed (---) boxes used to denote inclusion in mass balance determination.

Dry Solids, wt%	Residual Effective Alkali, g/L as Na_2O	Lignin, wt% on dry solids	Sugars/Acids, wt% on dry solids	Ash, wt% on dry solids	Organic/Inorganic, w/w
18.6 ± 0.9	6.4 ± 2.1	33.4 ± 5.4	15.9 ± 3.1	40.7 ± 2.2	1.2 ± 0.2

I. Spent liquor properties.

decoupling. All samples were analyzed at ambient temperature. The solvent, DMSO-d_6, peak is detected at 39.4 ppm.

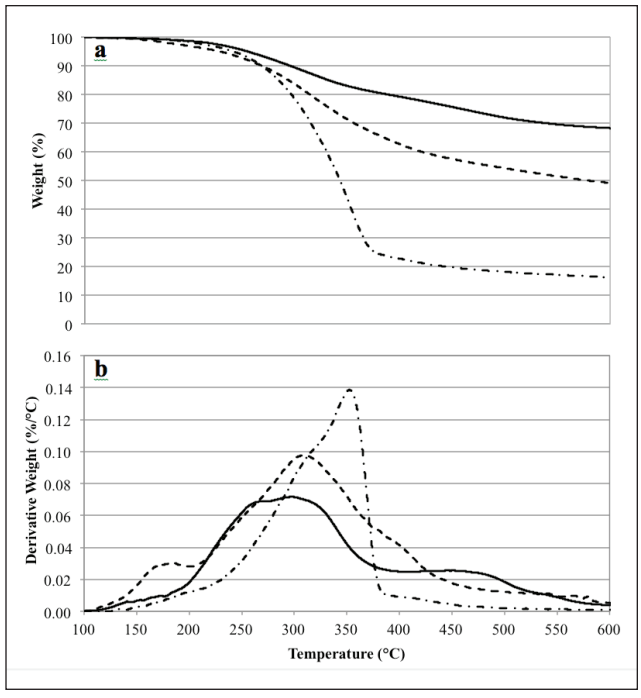
Char remaining after pyrolysis was ashed at 700°C in a muffle furnace until a constant weight and a grey inorganic residue (ash) remained to determine by difference the amount of carbonaceous residue formed during pyrolysis. The ash mass results were compared to sodium analysis, employing inductively coupled plasma optical emission spectroscopy (ICP-OES), conducted by the Analytical Laboratory and Maine Soil Testing Service at the University of Maine (Orono, ME, USA) and found to be in very good agreement with the ash being identified as pure Na_2CO_3.

H-factor, h	Pulp Yield, wt%	Rejects, wt%	Kappa Number
1014 ± 4	50.0 ± 2.1	0.8 ± 0.4	18.3 ± 5.6

II. Pulp properties.

RESULTS AND DISCUSSION

The average properties of the four soda-AQ spent liquors and of the pulps produced can be seen in **Tables I** and **II**, respectively. It can be seen that the lignin and sugars/acids content from the spent liquor samples have a significant amount of variation. While this may be a result of variation in



3. (a) Thermogravimetric analyzer (TGA) traces showing weight loss (%) as a function of temperature for sample 1 (–), Indulin AT (---), and pine sawdust (--·). (b) TGA traces showing derivative weight loss (%/°C) as a function of temperature. The derivative weight loss for pine sawdust has been reduced by a factor 5. All data points in graphs (a) and (b) have been normalized to allow comparison between samples.

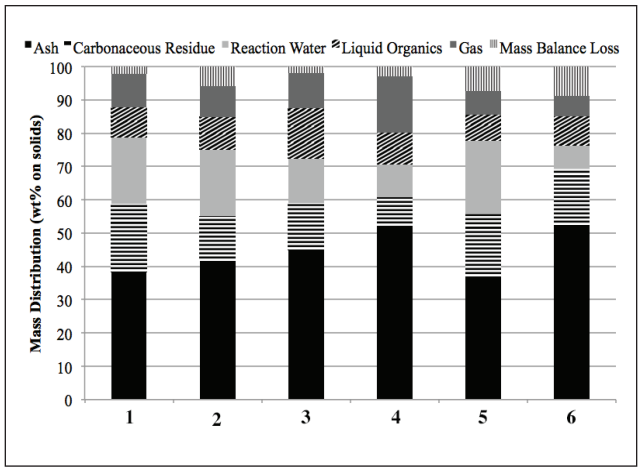
the testing methods used and/or process variability, it is believed for this work that the variation is caused by aging of the chips over the 9-month period during which the cooks were performed, even though the chips were stored in a cold room at 4°C.

Throughout the remainder of this paper, the spent liquor samples used for pyrolysis will be designated as follows where all HCOONa and NaOH charges are given as weight percent on spent liquor solids: **1**: spent liquor as is, **2**: spent liquor with 12.5 wt% HCOONa, **3**: spent liquor with 25 wt% HCOONa, **4**: spent liquor with 50 wt% HCOONa, **5**: spent liquor oxidized without NaOH, and **6**: spent liquor oxidized with 10 wt% NaOH supplementation. From the TGA data (**Fig. 3**), oven-dried sample **1** begins decomposing at around 100°C and proceeds through a two-stage decomposition regime: 100°C -375°C and 375°C -600°C ,with the former being more rapid and yielding more volatiles. The decomposition occurring between 100°C -375°C is likely that of the carbohydrates present in the spent liquor solids, as well as the initial decomposition of the lignin fraction. Lignin thermally decomposes over a very broad temperature range [36]; therefore, the second distinct decomposition from 375°C-600°C is likely that of the remaining lignin present in the spent liquor solids. A final mass loss of 28 wt% was observed at 500°C. This compares to a mass loss of 39 wt% in the kiln reactor observed for **1**. These results are in agreement with values reported in literature for fast pyrolysis of kraft black liquor, with the latter mass loss observed in the kiln reactor being slightly higher than the reported values. For example, Whitty et al. reported a mass loss of 29.5 wt% at 650°C for single-droplet pyrolysis of kraft spent liquor with a solids content of 64.4 wt% [18] and Gairns et al. reported a mass loss of 25-35 wt% at 500°C for fast pyrolysis of kraft spent liquor droplets with a solids content of 70 wt% [16]. Since volatilization yield increases with increasing heating rate [18,37], and pyrolysis in the present reactor setup takes place over a period of a few minutes at 500°C, the TGA mass loss represents a low estimate of the expected volatiles and NCGs generated in the present experiments. The ash content of the dry solids in spent liquor **1** is 40.7 wt%, which is much higher than precipitated low-sodium lignin (Indulin AT) or wood (represented here by pine sawdust), thus resulting in a lower devolatilization yield based on solids fed, as can be seen in Fig. 3. **Table III** compares the organic and inorganic content of these three feedstocks before and after pyrolysis at 500°C. While the devolatilization yield (i.e., mass lost) is the least for **1** and increases for Indulin AT and even further for pine sawdust, it can clearly be seen that the yield of carbonaceous residue is less for **1** compared to Indulin AT. The latter may be explained by the higher lignin and lower sugar content of Indulin AT than **1**. The last column in Table III shows that the amount of carbonaceous residue as a percentage of the organic content (100 – wt% of ash) of the feed is highest for Indulin AT and lowest for pine sawdust. This is a direct consequence of the high residual weight fraction of carbonaceous residue observed for lignin pyrolysis (~0.5) versus that of

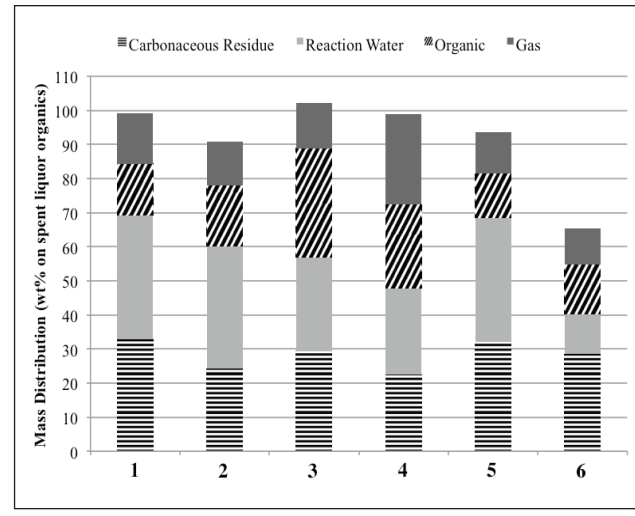
Sample	Composition			Mass Balances upon Pyrolysis at 500°C			
	Sugars, wt%	Lignin, wt%	Ash, wt%	Mass Lost, wt%	Char, wt%	Carbonaceous Residue, wt%	Carbonaceous Residue, wt% on organics pyrolyzed
1	15.9	33.4	40.7	39.2	58.8	18.1	30.5
Indulin AT	2.06[a]	90.0[a]	2.43[b]	62.0[b]	41.0[b]	38.6	39.5
Pine Sawdust	68.5[c]	27.7[c]	0.47[d]	86[e]	12[e]	11.5	11.6

[a] [39], [b] [26], [c] [40], [d] [41], [e] [42].

III. Comparison of various feedstocks demonstrating the effect of organic and inorganic content on the devolatilization yield and yield of carbonaceous residue upon pyrolysis.



4. Mass balances after pyrolysis for samples 1-6.



5. Yields based on spent liquor organics for samples 1-6.

hemicellulose (~0.2) and cellulose (~0.1) [38]. Since spent liquor contains a significant amount of sugar-derived organics as well as lignin, it is clear that it is more advantageous to use spent liquor as a feedstock for pyrolysis rather than precipitated lignin.

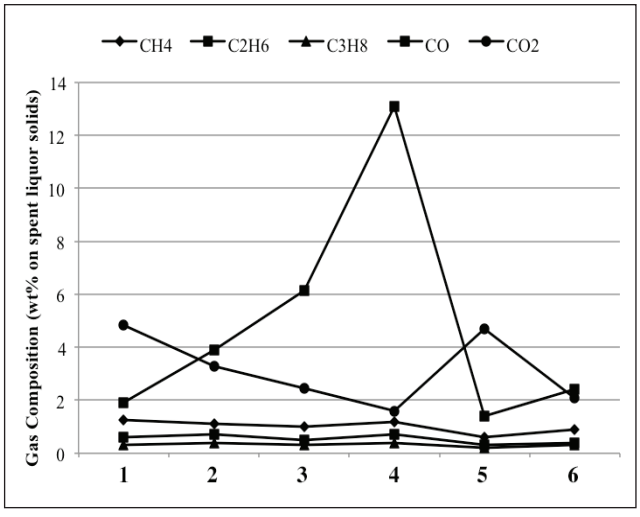
Mass balances after pyrolysis for the spent liquor samples were determined based on the total dry solids content of the feed (**Fig. 4**). Also noted in Fig. 4, the deviation from full mass balance closure is denoted as "Mass Balance Loss." The values of 1.7%-8.7% indicate that mass balance closure is relatively good when one considers the unavoidable mass losses due to handling. Reaction water is that which is formed during pyrolysis and does not include water present in the feed (i.e., aqueous mass as determined in Fig. 2 minus the water content in the black liquor feed). As can be seen from the data, the yield of liquid organics after extraction and evaporation of EtOAc increases from **1** to **3**, but subsequently decreases in the order **4**, **6**, **5** (Fig. 4 and **Table IV**). This suggests that addition of 25 wt% HCOONa on spent liquor solids (**3**) is the optimal loading to maximize the production of organics. It is also seen by comparing **1** – **4** that less reaction water (H_2O) is formed with increasing charges of HCOONa. This decrease in the formation of reaction H_2O suggests that the oxygen in the spent liquor is released more in the form of CO_2 and/or CO rather than in the form of H_2O. This shift may be catalyzed by the increase in the sodium cation (Na+) concentration with increasing HCOONa addition [43,44].

Since the ash content increases further as HCOONa is added prior to pyrolysis, or as NaOH is added to aid in oxidation prior to pyrolysis, the yield of the different fractions obtained upon pyrolysis (i.e., carbonaceous residue, liquid organics, reaction water, and gases) are also compared using as a basis the organics present in the original spent liquor feed, 59.3 wt% of spent liquor solids, thereby allowing a fairer comparison of the different feedstocks (**Fig. 5**). The yields of liquid organic material can also be seen in Table IV along with the respective pulp yields. The addition of HCOONa significantly improves the yield while oxidation reduces it. This is most notably seen for **6** (Fig. 5), which exhibits a much larger deviation from full mass balance closure. This may be explained by oxidation of a portion of the original spent liquor organics to CO_2 that is subsequently sequestered in the form of Na_2CO_3. In comparison to the Rinman process discussed previously [15], our process improves upon the yield observed in his work (60-70 kg/metric ton of pulp; Table IV) even with

Sample	Pulp Yield, wt%	Number of Pyrolysis Experiments Run	Yield[a], kg/metric ton of pulp	Yield[a], wt% on spent liquor organics
1	50.0	4	81.5	15.1 ± 2.1
2	48.5	1	105.7	17.8
3	48.5	2	162.8	32.0 ± 6.6
4	n.d.[b]	1	n.d.[b]	24.6
5	51.5	1	57.8	13.0
6	51.5	1	62.9	14.5

[a] Low-molecular weight organic compounds, [b] n.d.: not determined.

IV. Pulp yield and yield of organics after pyrolysis.



6. Gases evolved during pyrolysis for samples 1-6.

the original spent liquor (**1**) and more than doubles his observed yield when 25 wt% HCOONa is added (**3**). This suggests that pyrolysis is a superior processing technique when compared to dry distillation and the yield can be significantly improved with the addition of HCOONa.

The decrease in reaction H_2O formation from **1** – **4** was earlier attributed to more oxygen being removed as CO_2 and/or CO rather than as H_2O. However, a decrease rather than an increase in the CO_2 mass released is seen based on the measured composition of the gases (**Fig. 6**) as the addition of HCOONa is increased. The composition of the gases does show an increase in the amount of CO being generated with increasing addition of HCOONa, as would be expected for samples **1** – **4**. The thermal decomposition of HCOONa is as follows [33]:

$$2HCOONa \rightarrow Na_2CO_3 + H_2 + CO \quad (1)$$

There is, however, an increase in the CO mass released as the HCOONa addition is increased beyond that which is expected solely from HCOONa decomposition. This increase coupled with the noted decrease in CO_2 mass released could be explained by the following reaction [33]:

$$CO_2 + C \leftrightarrow 2CO \quad (2)$$

At the temperature of these pyrolysis experiments (500°C), however, it is unlikely that this reaction could occur even in the presence of a large quantity of Na^+. It is more feasible that the reverse water-gas shift reaction (Eq. [3]) is occurring due to H_2 being formed from HCOONa decomposition (Eq. [1]).

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad (3)$$

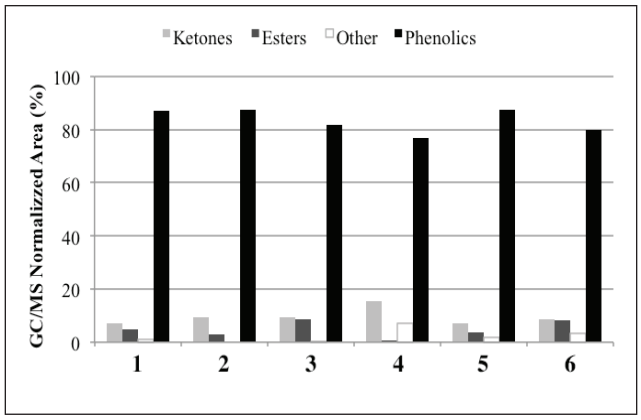
As would be expected [26], the reactive gases, CO and H_2, generated by thermal decomposition of HCOONa and released in situ decrease the carbonaceous residue (i.e., char) for **1** to **4** (Figs. 4 and 5), thus allowing for more organic carbon to remain in the organic layer. When the spent liquor is oxidized, with and without NaOH supplementation (**6** and **5**, respectively), the liquid organic yield is slightly reduced when compared to **1** (Figs. 4 and 5 and Table IV). Oxidation of the spent liquor prior to pyrolysis results in the formation of low-molecular weight compounds, such as phenolates and carboxylic acids that will be present as their respective sodium salts [31]. It has been shown that pyrolysis of the sodium salts of carboxylic acids results in the production of significantly deoxygenated aromatic compounds [45]. However, the organic yields for **5** and **6** are similar to that of **1**, and there is no significant increase in the evolution of CO and CO_2 for **5** as compared with **1** (Fig. 6), while the CO_2 evolution is lower for **6** than for **1**. Therefore, it appears that there is secondary oxidation to Na_2CO_3 of the primary low-molecular weight organic compounds formed during oxidation of the spent liquor organics, which eliminates the potential yield from these low-molecular weight compounds upon pyrolysis.

Methane (CH_4) through C_3 hydrocarbons comprise a small volume percent of the gas samples taken over the course of pyrolysis, with CH_4 being the most prevalent (0.6-1.2 wt% on spent liquor solids). As more HCOONa is added, the most prominent gas shifts from CO_2 to CO as would be expected based on the decomposition of HCOONa at elevated temperatures in an inert environment [27], while the amount of hydrocarbons remains relatively unchanged.

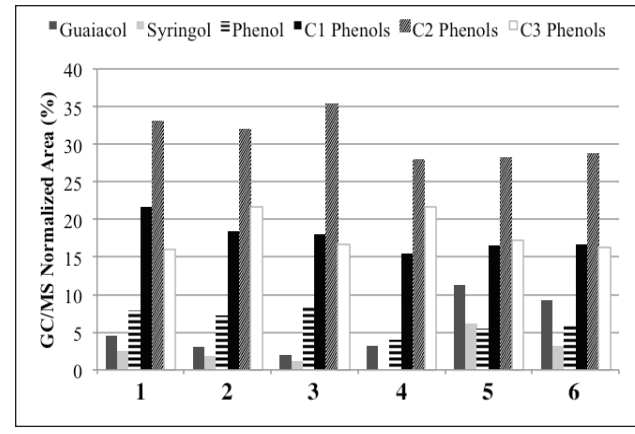
^{13}C NMR results of the organic product collected after pyrolysis (**Table V**) show that the primary products formed, irrespective of the feedstock used, are composed of aromatic structures (163-103 ppm) and alkyl hydrocarbon substituents (54-1 ppm), suggesting that only a minimal amount of oxygenated compounds are present. A nominal amount of

Type	1	2	3	4	5	6
Carbonyl	0	0	0	2	0	0
Aromatic	70	74	65	74	77	68
Methoxy/Hydroxy	1	1	1	1	8	18
Alkyl	28	24	34	22	15	14
Aromatic + Alkyl	99	98	99	96	92	82

V. Raw integrated areas (%) for carbon-13 nuclear magnetic resonance (^{13}C NMR) results for samples 1-6.

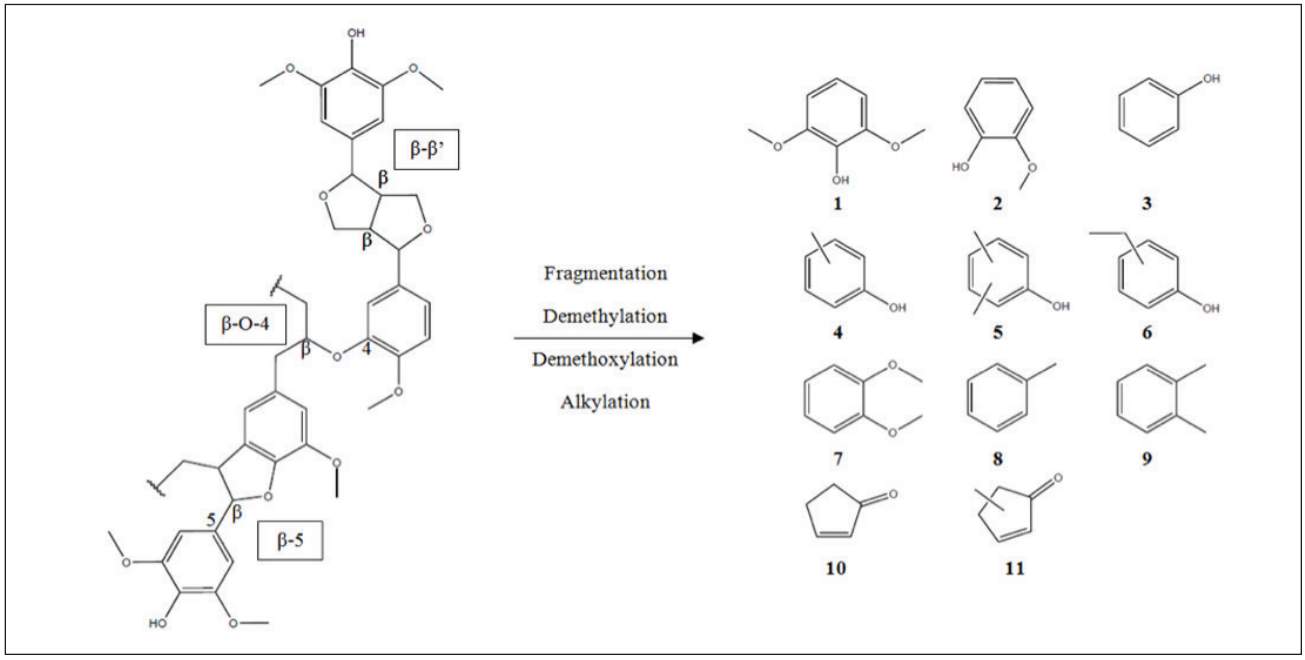


7. Gas chromatography-mass spectrometry (GC/MS) normalized chromatogram area showing the distribution of compound types present after pyrolysis for samples 1-6. Figure 8 shows a breakdown of the "phenolics" group based on their substituents.



8. GC/MS normalized chromatogram area showing the breakdown of the phenols based on their substituents for samples 1-6. C1: 1 substituent with 1 carbon bonded to the aromatic ring, C2: 1 or 2 substituents for a total of 2 carbons bonded to the aromatic ring, C3: 1–3 substituents for a total of 3 carbons bonded to the aromatic ring.

methoxy/hydroxy groups (70-54 ppm) are also present in the products for **1** - **4**, with an increasing amount being present in **5** and **6** likely due to the formation of a large quantity of highly oxygenated compounds resulting from oxidation. ^{13}C NMR of the aqueous layer shows only one peak at 49.2 ppm for all feedstocks and is likely methanol (MeOH) formed via demethoxylation reactions during pyrolysis. GC/MS data for the organic layer obtained after evaporation of EtOAc can be seen in **Figs. 7** and **8**. The data suggest that the predominant liquid organic products after pyrolysis are phenols with varying degrees of methylation and ethylation. This is in good agreement with the ^{13}C NMR data showing peaks between 163-103 ppm for carbons within the aromatic ring and peaks between 54-1 ppm for carbons from the ethyl- and methyl-substituents on the aromatic ring. The presence of a significant amount of phenolic compounds is desirable as they contribute less to bio-oil instability than acids and also increase the energy density of the organic fraction [44]. GC/MS indicates that there is unreacted guaiacol and syringol present in the organic product as well and as the HCOONa loading is increased, the relative abundance of each of these compounds decreases compared with **1**, suggesting that HCOONa plays a significant role in deoxygenation. As the HCOONa loading is increased (**1**-**4**), the relative phenolic



9. Proposed reaction scheme based on literature for the formation of substituted phenols from pyrolysis of soda-anthraquinone (AQ) lignin [46]. 1: syringol, 2: guaiacol, 3: phenol, 4: methylphenol, 5: dimethylphenol, 6: ethylphenol, 7: 1,2-dimethoxybenzene, 8: toluene, 9: o-xylene, 10: 2-cyclopentenone, 11: methyl-2-cyclopentenone.

content decreases, while the relative ketone content increases when compared with **1**, suggesting that HCOONa may promote the formation of cyclic ketones. Larger molecular weight compounds and molecular weight distributions were not investigated as part of this work.

One proposed reaction scheme for the pyrolysis of lignins isolated from alkali spent liquor consists of a consecutive two-step process: (1) cleavage of lignin interunit linkages, and (2) free-radical reactions that promote the formation of substituted phenolic-type compounds [46]. The present work supports this hypothesis as phenolics are the predominant product detected by GC/MS and ^{13}C NMR shows the presence of a large quantity of aromatic moieties. Phenolic-type compounds will be detected in the same shift region as aromatic moieties with ^{13}C NMR. A proposed reaction scheme for the formation of substituted phenols is presented in **Fig. 9**. The presence of these products shows that there is also a significant amount of demethoxylation occurring at the temperature used in this study, suggested by the comparatively small presence of guaiacyl and syringyl moieties when compared with phenols. This is in contradiction to previous work, which shows that demethylation reactions are more energetically favored in comparison to demethoxylation reactions and are minimal at temperatures at and below 500°C [46]. It has been suggested that the presence of the Na+ cation has a catalytic effect on the compounds observed after pyrolysis of alkali lignins, enhancing demethoxylation over demethylation for guaiacyl moieties and promoting decarboxylation and dehydration reactions, which is in agreement with the MeOH observed from ^{13}C NMR, the phenols observed with GC/MS and ^{13}C NMR, and the formation of H_2O [47]. The occurrence of demethoxylation reactions is also supported by the lack of secondary hydroxyl groups observed by GC/MS on the aromatic moieties.

CONCLUSIONS

The present work demonstrates that pyrolysis is a superior processing technique to dry distillation for producing low-molecular weight organic compounds from soda-AQ spent liquor that phase separates from the aqueous layer. The addition of 25 wt% HCOONa yields the highest organic content (32 wt% on spent liquor organics, or 163 kg low-molecular weight organics per metric ton of pulp produced), while oxidation of the spent liquor prior to pyrolysis has a detrimental effect on the organic yield and results in a product with significant oxygen content. The major products observed for all spent liquor samples were phenols with varying degrees of methylation and ethylation; however, as the HCOONa addition was increased, a decrease in phenols was observed alongside an increase in ketones. These phenols have the potential to be employed as renewable building blocks for the production of value-added products such as polycarbonates, epoxy resins, and nylon, among many others. GC/MS results, supported by ^{13}C NMR results, suggest a significant amount of deoxygenation can be realized by performing pyrolysis on spent liquor with HCOONa addition. **TJ**

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ABOUT THE AUTHORS

We chose to research this topic to provide alternative feedstock options for the production of bio-based fuels and chemicals from excess spent pulping liquor as we move towards a mill-based biorefinery that produces more and improved traditional pulp and paper products as well as biochemicals and fuels.

Much of the research that has focused on pyrolysis of spent pulping liquor has been undertaken to gain a better understanding of the pyrolysis and combustion processes occurring in the recovery boiler. We, on the other hand, aim to demonstrate the potential for production of new value-added products by pyrolysis of excess spent pulping liquors at different optimal operating conditions.

The most challenging aspect of this research was determining the thermochemical conversion technique that would provide us with the most accurate mass balance information, as well as optimal conditions for the production of a bio-oil from spent pulping liquor. By trial-and-error using different thermochemical processing techniques, we decided that the utilization of the kiln reactor for this research would provide us with the desired pyrolysis and product information.

The most interesting information gleaned from this research is that the addition of sodium formate to spent pulping liquor significantly improves the bio-oil yield without significantly influencing the bio-oil composition. One of the most surprising findings in this research was the lack of methoxy substituents present in the bio-oil as observed using both GC/MS and ^{13}C NMR, considering the use of hardwood and the thermodynamic stability of the bond between the aromatic carbon and the oxygen of the methoxy group.

St. Pierre

van Heiningen

Beis

This research is intended to demonstrate that an additional revenue stream is possible at a mill by utilizing a portion of the spent liquor stream for the production of value-added products while reducing the load on the recovery boiler, which ultimately can lead to an increase in pulp production.

Building upon the findings presented in this manuscript, we intend to utilize concentrated spent pulping liquor as is sprayed into a commercial recovery boiler, and to consider fluidized bed fast pyrolysis as a more practical pyrolysis operation.

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