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Characterization Of Kraft Alkali Lignin And Products Of Its Thermal Degradation By Fractional Pyrolysis Methods

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CHARACTERIZATION OF KRAFT ALKALI LIGNIN AND PRODUCTS OF ITS THERMAL DEGRADATION BY FRACTIONAL PYROLYSIS METHODS

by

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This thesis, submitted by Keith M. Voeller in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota, has been read by the Faculty Advisory Committee under whom the work has been done and is hereby approved

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PERMISSION

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Keith Michael Voeller

December 2nd, 2015

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ABBREVIATIONS

Abbreviations	Full Meaning
DCM	Dichloromethane
DSC	Differential Scanning Calorimetry
FID	Flame Ionization Detector
G	Guaiacyl
H	p-Hydroxyphenyl
ID	Internal Diameter
IS	Internal Standard
LC	Liquid Chromatography
LLE	Liquid-liquid Extraction
m/z	Mass to Charge Ratio
MeOH	Methanol
MS	Mass Spectrometry
MW	Molecular Weight
NIST	Nation Institute of Standards and Technology
PAH	Polyaromatic Hydrocarbons
PM	Particulate Matter
ppm	Parts per Million
rpm	Revolutions Per Minute
S	Syringyl
TCA	Thermal Carbon Analysis
TD-Py-GC-MS	Thermal Desorption-Pyrolysis-Gas Chromatography-Mass Spectrometry
TGA	Thermal Gravimetric Analysis
UV	Ultraviolet
wt. %	Weight Percent

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ABSTRACT

At present, methods addressing the characterization of lignin and its decomposition products are limited. Typical approaches reported various spectroscopic, chromatographic and thermal methods. None of the methods is ideal for different reasons. In this study, a novel thermal carbon analysis (TCA) was developed providing essential mass balance data complementary to liquid-liquid extraction (LLE) prior to separation and identification by gas chromatography and mass spectrometry (GC-MS) as well as thermal desorption-pyrolysis-gas chromatography-mass spectrometry (TD-Py-GC-MS) to fully characterize lignin and its degradation products from hydrothermal treatment in subcritical water conditions.

The TCA method enabled a quantitative thermal evolution profile through TD and pyrolytic temperatures (up to 890 °C) with and without oxygen. Mono- and diaromatic compounds were used as model compounds to optimize operating conditions. Sample introduction was explored by investigating the effects of solvents, loading matrices, amount of sample loaded as well as the effect of initial temperature steps.

A multistep temperature ramp was then evaluated and applied to untreated lignin where up to 55 wt.% evolved under the presence of oxygen as black carbon (i.e., coke) and a mass balance closure of 94.8 ± 5.5 wt. % was achieved. Analysis of lignin by TGA with a similar heating ramp to TCA showed a comparable mass distribution throughout the thermal profile; however, TCA has the advantage of being selective for carbon.

The developed methods were employed to characterize lignin degradation products. Lignin was hydrothermally treated using an analytical static batch reactor at temperatures between 200 – 300 °C. The products were then analyzed by TCA, liquid-liquid extraction (LLE)-GC-MS, and also TD-Py-GC-MS. TCA was used to provide overall product characterization based on the evolution temperature and LLE-GC-MS showed a strong correspondence with the products evolving at 200 and 300 °C by TCA and GC-elutable organic compounds. TD-Py-GC-MS allowed for the differentiation of monomeric species evolving at low temperature steps (200 and 300 °C) from large molecular weight species pyrolyzed at 400 – 870 °C. TD-Py-GC-MS product identification were complementary to thermal profiles obtained by TCA.

CHAPTER I

INTRODUCTION

I.1 Lignin: Occurrence and Chemical Structure

As the world's fossil fuel reserves continue to deplete, petroleum prices increase as well as the need for new biofuels and biochemicals. Lignocellulosic biomass is currently being targeted as a potentially economical option for a wide range of industrial applications. This biomass is composed of three major components: cellulose, hemicellulose and lignin.[1] Cellulose and hemicellulose are polysaccharides that can be hydrolyzed and then fermented to valuable products such as ethanol.[1] The third major component, lignin, accounting for 15 to 40% of dry biomass, fills the spaces in the plant cell wall between cellulose and hemicellulose and acts as the 'glue' that gives plants their structure.[2] Lignin is a major component of wood and grass; it has also been discovered as being widely distributed in fruits, seeds, bark, roots, pitch, cork and seaweed cells.[3] This broad range of sources makes lignin the second most abundant naturally occurring polymer after cellulose.[3, 4, 5, 6, 7] At present, 50 million tons of lignin are produced annually, primarily as a byproduct from the ethanol and paper industries.[3, 4, 5, 8] Lignin utilization has been studied as a potential source of value added materials such as bulk chemicals, thermoplastics and carbon fibers.[5]

The paper industry is the largest producer of lignin. The most common methods of lignin production such as the kraft, lignosulfonate and soda pulping processes.[1, 2, 9, 10, 11] Only ~2% of lignin produced from the paper industry is commercially available, which

consists of 630,000 tons of kraft lignin.[12] Biorefineries also have the potential to produce significant amounts of lignin from lignocellulosic biomass pretreatment. The US Department of Energy estimates up to 225 million tons of lignin to be produced from 750 million tons of biomass.[13] These pretreatments include steam explosion, acid and alkali pretreatements, organosolv, ammonia fiber explosion and ionic liquid dissolution. [1, 14] Multiple biomass pretreatments that are used to isolate lignin from the biomass may cause chemical alteration, such as the incorporation of sulfur.[15]

The focus of this study is on lignin isolated from the Kraft process, currently the dominant global process for production of lignin, accounting for about 90% of its production, Kraft lignin is commercially available from both Sigma Aldrich and MeadWestvaco.[2, 11, 15] During this process, lignin is isolated through dissolution using sodium hydroxide. After being exposed to high pH, 13 – 14, the solution is introduced to elevated temperatures, up to 170 °C, forming alkali-soluble lignin, which is separated from the solid content.[11, 15] Acidification by mineral acids is then used to precipitate lignin and isolate it from wood degradation products such as cellulose, proteins or other sugars.[11]

Lignin is a complex three-dimensional non-regular polymer, formed by the polymerization of phenylpropanoid monomers, which give rise to *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) phenylpropanoid units linked together by C-C or C-O-C bonds (Figure 1).[16, 17] The molecular mass of isolated lignin is typically in a range of 1,000-20,000 g/mol but is challenging to determine since lignin unavoidably fragments during pretreatment processes.[10]

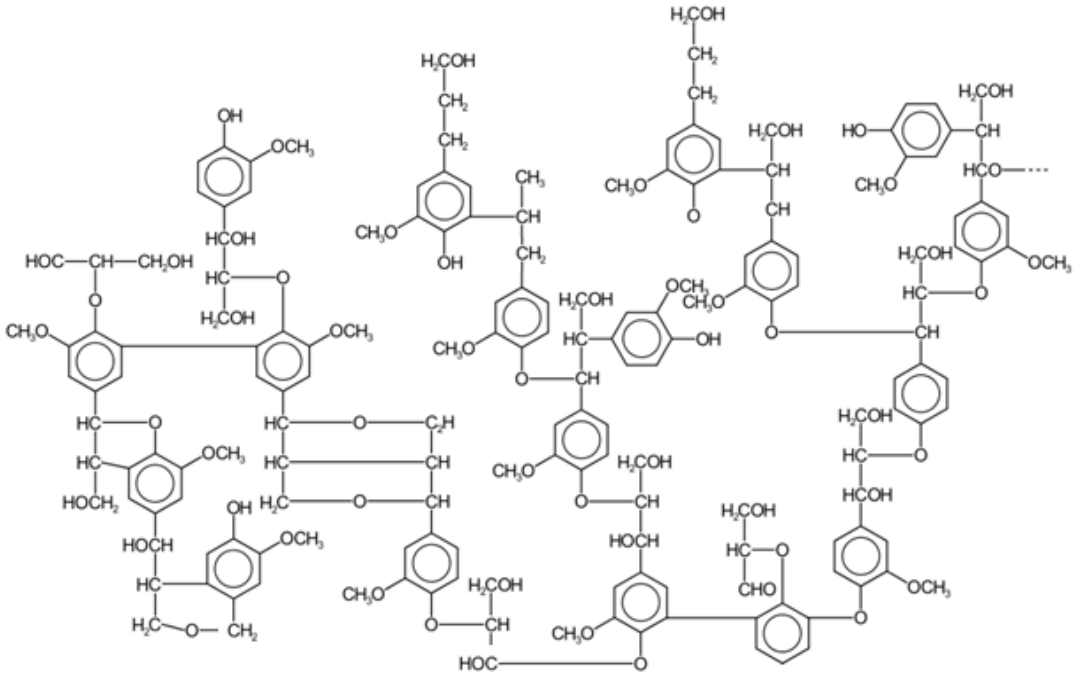


Figure 1. Partial structure of representative lignin molecule.[17]

The same structural features of lignin, which allow for structural stability of the plants, cause its chemical recalcitrance. Efficient utilization of lignin is an extreme challenge due to the diversity of functional groups for monomeric units as well as complex covalent bonds network throughout lignin.[18] Since lignin is an abundant polyphenolic structure, it appears to be an ideal feedstock, through depolymerization, for production of fuel and low molecular weight aromatic, phenolic and miscellaneous monomers.[13, 19] There are multiple ways to depolymerize lignin, which include but are not limited to biological methods using either microorganisms or enzymes, and thermochemical by pyrolysis, chemical oxidation, hydrogenolysis, gasification, and hydrolysis under supercritical conditions.[2] Nevertheless these methods are either not as effective or require aggressive reagents, thus there is ongoing need to develop and study new promising processes. None of them leads to an efficient degradation of lignin, which may be limited by the researchers' ability to characterize lignin and its degradation products.

I.2 Chemical Characterization

Due to complex composition and structure, the degradation of lignin is strongly influenced by its reaction temperature and heating rate.[9] These conditions affect a large domain for temperature degradation, conversion and product yields, thus emphasizing the need for a comprehensive characterization method for lignin and degradation products.[9]

Typical approaches for the chemical analysis of lignin and its degradation products may be divided into two categories: methods characterizing the bulk properties of lignin such as spectroscopic methods of nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared spectroscopy (FTIR); and separation methods targeting individual constituents including size-exclusion (SEC), gas (GC) and liquid (LC) chromatography, usually coupled with mass spectrometry (MS). Due to lignin recalcitrance, thermal methods are also used to provide information about the sample as a whole, such as thermal gravimetric analysis (TGA) or targeting specific constituents, e.g., pyrolysis-GC-MS (Py-GC-MS).[10, 16, 20, 21, 22] These analytical methods are often performed in combinations to achieve a more comprehensive characterization. Each method comes with its own advantages and disadvantages discussed below in detail.

Spectroscopic methods are attractive for the analysis of lignin and its degradation products as they are non-destructive and provide sample characterization as a whole. NMR and FTIR give insight on lignin as a macromolecule, revealing aromatic units and inter-unit linkages as well as provide details about different functionalities of lignin and degradation products.[16, 21, 22] However, spectroscopic methods cannot readily distinguish between the initial lignin and its degradation products as the same types of specific bonds and functionalities may be present making quantification difficult.[14]

Chromatographic methods allowing for the separation of lignin from its degradation products include SEC typically with ultra-violet (UV) or refractive index detection, or GC and LC with identity typically being further confirmed by mass spectrometry.[10, 14, 16, 18, 23, 24] SEC is often used for the determination of molecular weight of lignin and the mass distribution of degradation products.[10, 16, 24] Polystyrene standards are typically used for the determination of masses by SEC; however, these standards are not an adequate representation of lignin and its degradation products due to the irregularity of the lignin macromolecule and differing functionalities.[24] Thus differences in chemical structures add to stationary phase interactions (those beyond the size exclusion effect) characteristic for polar polymers, e.g., lignin.

Another frequently employed chromatographic method is GC-MS analysis following the sample preparation using liquid-liquid extraction (LLE) of lignin degradation products.[14, 18] Although this method is an excellent tool for identification of various species, it is limited by volatility of the analytes and LLE efficiencies, as it characterizes only an extractable GC-elutable fraction, i.e., phenolic monomers and some dimers. While this fraction is most desirable as phenolic monomers are considered high value-added chemicals, it often represents only a small portion of the overall carbon balance.[25] LC-MS, typically with electrospray ionization, seems to be more promising than SEC and GC for characterization of lignin and its degradation products, as it more accurately analyzes the soluble fraction as a whole using lignin model compounds as standards.[23] However, this method is not well-suited for application to unknown products due to selective ionization, fragmentation (loss of molecular ions) and limited commercial availability of chromatographic standards. Although some fragmentation issues were recently resolved

for monomers and dimers, this method still cannot be readily applied for screening of lignin oligomeric degradation products, for which identification and quantification standards are not readily available.[23]

Thermal analysis protocols may be considered as a separate category of methods used for lignin and its degradation products characterization. Py-GC-MS provides a comprehensive characterization of lignin and its degradation products enabling relatively fast analysis.[4, 16, 26] The majority of Py-GC-MS studies heat the sample in an inert atmosphere in a range of 400 – 1000 °C (typically 600 – 800 °C).[22] Single step pyrolysis is used for determination of syringol/guaiacol (S/G) ratios in lignin to classify the hardness of wood[8, 20, 21, 26, 27, 28] as well as identifying compounds from degraded lignin samples.[3, 6, 7, 25, 29, 30] However, a limitation of using this single pyrolysis step setup is that monomers cannot be distinguished from the less desirable products of higher molecular weight oligomers. In addition, products of single step pyrolysis are merely semi-quantified based on normalized peak areas.[3, 21, 26, 28, 29] Only a few pyrolysis studies used calibration standards for product quantification but this method does not distinguish monomers and higher MW (molecular weight) species.[6, 7, 8, 20, 27]

To obtain a better understanding of the structure of lignin and its degradation products, fractional Py-GC-MS methods have been performed more recently, in which products could be seen evolving at several sequential temperature steps (400 – 1050 °C) to investigate changes in S/G ratios of products or quantities of liquids and non-condensable gases.[5, 31] Pyrolytic, i.e., bond-breaking, conditions are considered to occur above 400 °C in an inert atmosphere. Lignin, however, has been shown to thermally degrade at temperatures as low as 230 – 260 °C.[9] Therefore fractional lignin degradation has been

investigated at temperatures below pyrolytic conditions; i.e., conditions generally considered as thermal desorption (TD).[32, 33] Thermal desorption (TD) steps have been integrated into fractional pyrolysis methods to include products that may be formed at temperatures below pyrolytic conditions.[34, 35, 36, 37, 38] Although exploration into lower temperatures has given a greater understanding of lignin degradation, quantification is still lacking and so only normalized relative product yields are routinely reported. By analyzing fractional thermal desorption and pyrolysis ranges, monomers can be distinguished from similar products resulting from the thermal degradation of oligomers and polymers, e.g., lignin itself. TD-Py-GC-MS analysis of lignin and its thermal degradation products is also limited to its volatilizable (upon pyrolysis) fraction thus not accounting for any coked product that does not evolve onto the column.

Thermal gravimetric analysis (TGA) in combination with differential scanning calorimetry (DSC) or Fourier transform infrared spectroscopy (FTIR) is used for the analysis of the reaction system, to provide insights on the degradation mechanism during pyrolysis, and also to determine the thermal stability of isolated lignin.[4, 16, 39] Rapid analysis for biomass characterization by TGA is used to show compositional differences in samples.[40] TGA monitors mass loss as a function of temperature while DSC measures heat flow providing melting enthalpies of lignin decomposition.[3, 16] Both of these methods provide an overall sample characterization; however, they do not provide any insight into the specific chemical structure of lignin and products of its degradation. TGA is not able to distinguish lignin from impurities resulting from its isolation from biomass; e.g., salts from alkali treatment or any sulfur containing compounds.

To our knowledge, analysis methods selective for carbon have not been applied to lignin and its degradation products, with the exception of total carbon determination through elemental analysis. This is unlike other fields of chemistry characterizing different matrices, such as atmospheric particulate matter (PM) or soil, which distinguish between organic and black carbon.[41, 42, 43] This is expected as all of the carbon present in lignin is of organic nature. At present, a standard method for the characterization of PM employs thermal optical analyzers evolving carbon in the temperature range up to 890 °C with and without oxygen using a methanizer with sequential flame ionization detection (FID). Differentiation of organic and black carbon (in these studies termed as elemental carbon) is obtained using an optical feature. While the optical feature is not useful for determination of organic molecules such as lignin, thermal profiles with and without oxygen may provide significant input on the overall composition of lignin and its degradation products particularly because it is known that after the thermal treatment of lignin in anaerobic conditions, a significant portion (~20 wt. %) analyzed by TGA remains even though it is organic carbon based.

In this study we hypothesized that the combination of thermal methods and carbon analysis has significant potential in characterization of lignin as well as lignin degradation products allowing for differentiation of organic carbon (i.e., volatile monomeric compounds, oligomeric fraction and the fraction ultimately yielding coke) while still obtaining structural characterization of the products. Thus the aim of this study was to develop a comprehensive yet simple thermal carbon analysis (TCA) method, which would provide a quantitative thermal evolution profile through thermal desorption and pyrolytic temperatures with and without oxygen. In this study the TCA conditions were optimized

for an analysis suitable for analytical characterization of lignin and its degradation products obtained from hydrothermal treatment. The thermal temperature profiles were evaluated using standard compounds as well as untreated lignin with a goal to minimize the coke formation caused by pyrolysis and allow differentiation between the species evolved during TD steps and at pyrolytic temperatures. Essential parameters, such as the impact of solvent or sampling surface were evaluated. The method was then applied to various lignins and lignin degradation products evaluated in comparison to TD-Py-GC-MS and TGA, which served as a reference method.

A novel approach to the analysis of lignin and its degradation products can be taken by using a slightly modified thermal carbon analysis (TCA) method without the optical features. TCA enables quantitative characterization of both lignin as a macromolecule and its degradation products allowing for differentiation of different types of carbon (i.e., volatile monomeric compounds, oligomeric fraction and fraction ultimately yielding coke) while still obtaining structural characterization of the products. Ideally TCA will improve the fractional analysis of both lignin and its thermal degradation products compared to TGA as it is selective to carbon, not influenced by impurities, as well as characterizes the whole sample including any coked product.

CHAPTER II

STATEMENT OF PURPOSE

The goal of this study is to develop a TCA method providing mass balance closure on carbon for the whole sample, both for lignin and lignin degradation products. The advantage of the TCA method is that it can provide a quantitative profile for small molecular weight (MW) compounds evolving at 200 and 300 °C, as well as large MW compounds being pyrolyzed and evolving at temperatures above 400 °C and finally a typical unquantified portion of carbon, labeled in this study as a coked fraction, may be evolved only after the addition of oxygen. Our goal is to develop a temperature program, which would evaluate various factors including the effect of sample loading (e.g., solvent, loading surface, amounts of carbon loaded) as well as temperature profiles providing information on different fractions of carbon as well as minimizing the coked portion of the carbon. These fractions can be further identified by complementary analysis with TD-Py-GC-MS.

CHAPTER III
EXPERIMENTAL METHODS
III.1 Materials

Solvents used included dichloromethane, DCM; and methanol, MeOH (VWR, Arlington Heights, IL, USA), which were GC and HPLC grade respectively; as well as deionized water obtained from a Direct-Q 3 UV system purifier (Millipore, Billerica, MA, USA) with the total organic carbon content below 5 ppb (manufacturer specification). ACS grade sucrose used for calibration of the thermal carbon analyzer instrument was obtained from Alfa Aesar (Ward Hill, MA, USA). Standards used for method development, guaiacol (98%), syringol (99%), levoglucosan (99%), vanillin (99%) and pinoresinol (≥ 95%) were all purchased from Sigma-Aldrich (Milwaukee, WI, USA). Divanillin used for method development was synthesized previously using a published protocol[44] Its purity was not quantified; but it was assessed semi-quantitatively by GC-MS analysis, where only a small fraction of vanillin was present. Alkali lignin used for the hydrothermal treatment of lignin was also purchased from Sigma-Aldrich (Milwaukee, WI, USA). Lignin contained 64.03%, 5.62%, 0.43% and 1.36% C, H, N and S respectively (Atlantic Microlab Inc, Norcross, GA, USA) with a moisture content of 3.9% (Appendix VII).

III.2 Thermal Carbon Analyzer

The instrument used in this study was a thermal optical analyzer purchased from Sunset Laboratory Inc. (Tigard, OR, USA) equipped with a flame ionization detector (FID). A Pall Flex 2500QAT-UP tissue quartz filter (Pall Corp, East Hills, NY,USA) was

used for analysis. For the purpose of this study, the optical feature was neglected, hence the term thermal carbon analysis or TCA.

Theory of Operation

The method used is a National Institute for Occupational Safety and Health, NIOSH, approved method for the determination of carbon in aerosol samples.[45] The thermal carbon analyzer, TCA, is a method that submits the sample to a programmable temperature profile while all evolving products are quantitatively converted to CH_4 and measured by a flame ionization detector, FID. The individual steps of the process are outlined in the schematic diagram, Fig. 2.

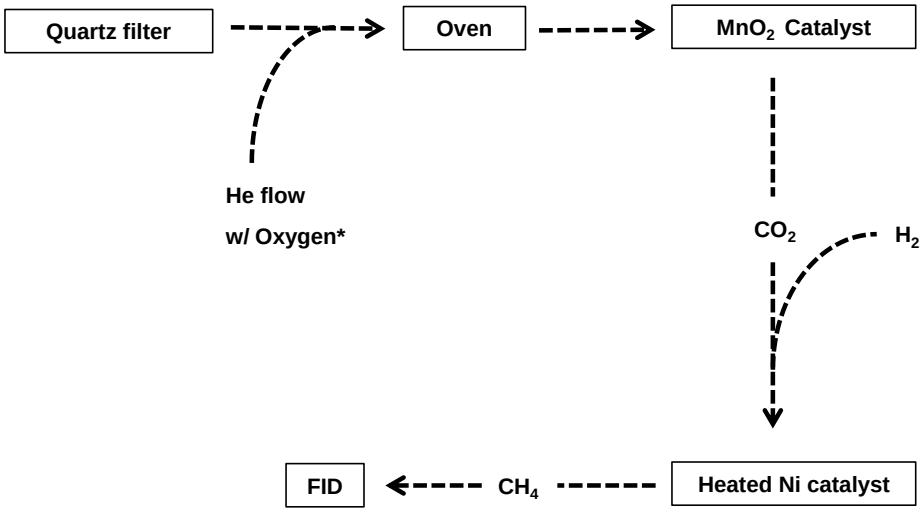


Figure 2. Schematic diagram of the thermal carbon analyzer.*Oxygen is added after the sample is heated and then cooled down to 550 °C before heating back up.

First, the sample was placed into the oven, typically spiked on a quartz filter, and then the system was purged with He followed by the desired temperature steps, specifics on times and heat ramp are provided below. Thermally desorbing compounds (200 – 300 °C) and pyrolyzed products (> 400 °C) flowed over a heated MnO_2 oxidizing catalyst and were quantitatively converted to CO_2 gas. The CO_2 was then swept out of the oxidizing

oven and mixed with hydrogen gas prior to flowing through a heated Ni catalyst where it was quantitatively converted to CH_4 and subsequently measured using a FID. After the initial ramp, the oven was cooled and the flow stream switched to an oxidizing He/O_2 (10% O_2) carrier gas mixture followed by a second temperature ramp. After the second programmed temperature ramp finished, a known amount of methane was introduced into the TCA automatically for an internal calibration. During the second heating step, any coked products are oxidized and detected similarly to the organic carbon. To quantify carbon evolving at different temperatures, a calibration using sucrose and water was used by integrating peak areas (see Appendix I).

Fig. 3 shows an example of a thermogram of lignin analyzed by the TCA with a stepped temperature ramp. Initially an inert atmosphere is used before the sample is cooled to 550 °C when O_2 is introduced.

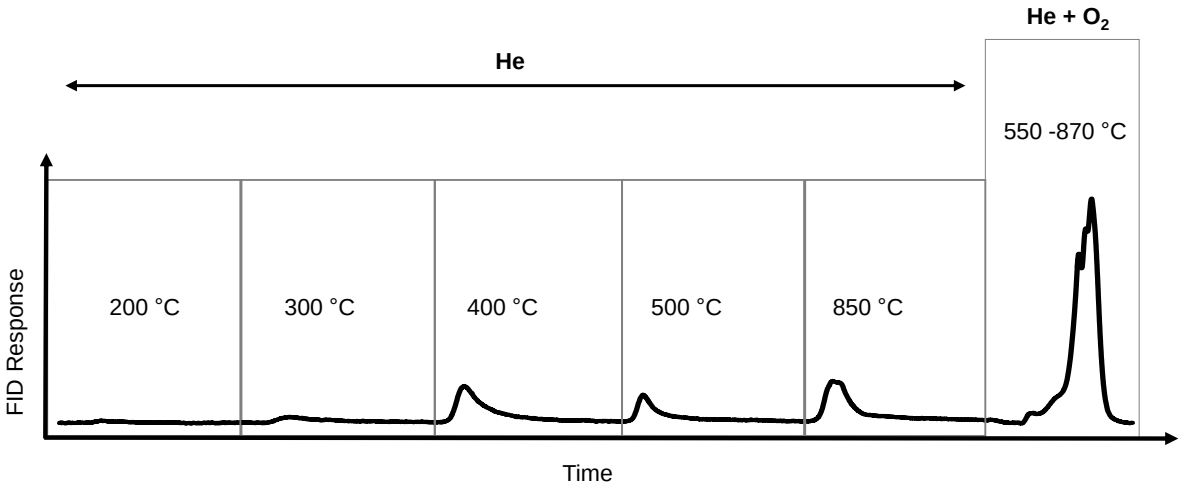


Figure 3. Example of thermal profile of sample acquired from TCA. During the first heat ramp only He is used before cooling down and heating again with the addition of O_2.

To integrate the data, a secondary program was used. OriginLab® Origin Pro 9.1 was used for peak integration to the baseline adjusted for the signal of the FID response.

Once integrated, the carbon evolving at different temperatures could be quantified based on a calibration using sucrose by integrated peak areas (see Appendix II).

TCA Experimental Conditions

The initial evaluations were performed on standards (low MW compounds representing lignin 'monomers') typically introducing 10 µL of the solution containing 7 µg of C. Syringol was dissolved in H_2O, MeOH, and DCM. Prior to introduction to the oven, all samples were dried at 40 °C for 4 min with the exception of water samples which were dried for 7 or optionally 8 minutes. Similarly, syringol was introduced onto a glass boat either directly or using a standard approach on a quartz filter and dried the same way.

The effect of carbon loading on the TCA was evaluated by loading lignin standards in a range from 0.1 to 20 µg C. Guaiacol and vanillin were dissolved in DCM while pinoresinol was dissolved in MeOH. This experiment used the same protocol for the TCA as the study investigating different effects of solvent with syringol described in the previous paragraph. The samples were heated with sequential steps of 200, 300, and 700 °C for 2 min under He atmosphere and then cooled down to 550 °C, after which O_2 was introduced to the sample which was then heated to 870 °C with a heating rate of 5 °C s^{-1}.

The effect of the initial temperature step was evaluated based on the analysis of lignin standards. Syringol, guaiacol, and vanillin were all dissolved in DCM; pinoresinol was dissolved in MeOH; and divanillin was introduced directly onto the quartz filter due to solubility difficulties. The initial temperature step was varied between 100, 200, and 300 °C followed by 300 °C (except if the initial step was 300 °C) and followed the same method as mentioned above.

Lignin was also evaluated using different temperature protocols ranging with TD conditions 100, 200 and 300 °C and pyrolysis temperatures 400, 500 and 870 °C, the final pyrolysis in presence of oxygen was at 890 °C. Each temperature step was held for 5 min with a heat rate of 5 °C s^{-1} between temperature steps.

III.4 TGA

A SDT Q600 TGA (TA Instruments, New Castle, DE, USA) was operated with the use of N_2 at a flow rate of 20 mL/min. Alkali lignin (approximately 20 mg) was analyzed with a temperature ramp of 25 °C/min between steps of 200, 300, 400, 500 and 850 °C, each of which was held for 5 minutes. The experiment was performed in triplicate.

The data were integrated by determining the wt. % of lignin evolved during the temperature ramp until the time the isothermal step was finished; i.e., from the time when the TGA started ramping from 300 to 400 °C until isothermal conditions were held at 400 °C for 5 minutes. The amount of mass remaining after the analysis was considered to be the coked fraction.

III.5 Analytical Static Batch Reactor

The small volume static batch reactor, Fig. 4, was designed and constructed for analytical purposes to be used for the hydrothermal treatment of lignin. The purpose of the static batch reactor was to be able to treat lignin with subcritical water and various catalysts to optimize its degradation.

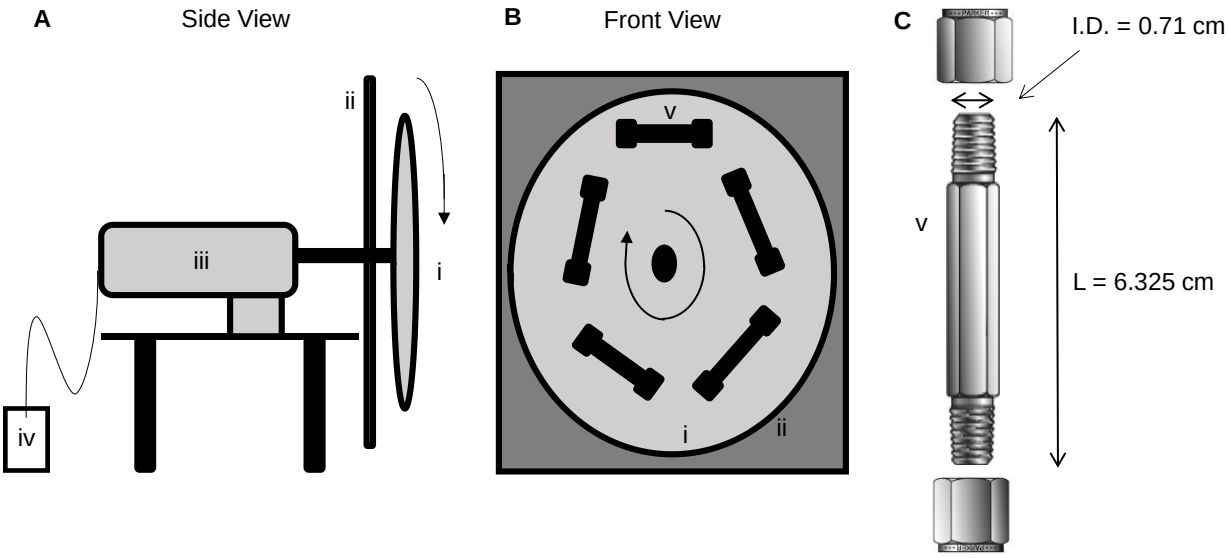


Figure 4 Schematic diagram of the analytical static batch reactor. Panel A is a side view where i is the rotating disc, ii is the steel plate plugging the GC, iii is the electronic motor driving the shaft, iv is the speed controller. Panel B represents a front view showing the placement of the vessels (v) on the rotating disc (i). Panel C is a diagram of the vessel.

The reactor consisted of an electric motor, Fig. 4.iii, that was mounted on top of a stainless steel stand. A speed controller, Fig. 4.iv, was used to adjust the angular speed measured as revolutions per minute (rpm) of the rotating stainless steel disc, Fig. 4.i. Small clips were used to attach individual reactor vessels, Fig. 4.v, to the rotating disc. A 1/4 inch stainless steel plate, Fig. 4.ii, was covered with insulation to serve as a door while the reactor was positioned tightly against a gas chromatography oven. Up to 5 independent experiments could be run during one reaction experiment for repeatability.

The vessels were purchased from Park (Mandan, ND, USA). The main body of the stainless steel vessel, Fig. 4.C, had an internal diameter of 0.71 cm with a length of 6.325 cm and a total volume of 4.65 mL with two threaded caps on each end (volume calculation can be seen in Appendix III). The caps were secured and sealed using polytetrafluoroethylene thread tape. According to factory specifications, the vessels were pressure rated to 7500 psi (517 bar).

Due to volume restrictions, a pressure gauge could not be conveniently installed as the void volume of the union would be significant compared to the total vessel volume. To insure safety, pressure calculations were performed to not exceed the limit. The calculations, which can be seen in Appendix IV, use the density of water and National Institute of Standards and Technology (NIST) water saturation points at varying temperatures, which and calculated to at least 82% liquid phase inside the vessel.

To determine the difference in temperature inside the vessel against the GC oven due to heat transfer resistance of the stainless steel vessel walls, a thermo-couple was placed inside a reference vessel using a union. A comparison between the oven temperature and vessel temperature can be seen in Appendix V. The difference between the two temperatures was noted during hydrothermal treatment experiments for lignin.

Experimental conditions for amounts of lignin and water used at each temperature can be found in Appendix IV along with respective calculated pressures and liquid phase fraction.

III.6 LLE-GC-MS

To collect the entire sample from the vessel, each vessel was rinsed with H_2O to a final volume of ~7 mL. LLE was performed on a 1.00 mL of rinsed sample taken. To this 1.00 mL of sample, 50 µL of 4-chloroacetophenone (10,000 µg/mL), used as a recovery standard, was spiked. Next, 1.00 mL of DCM was added and the mixture was vortexed for 1 min. The DCM phase (bottom) was collected and the extraction step was repeated 2 more times totaling in 3 mL of DCM extracts. Last, 75 µL of *o*-terphenyl (10,000 ppm), used as

an internal standard (IS), was spiked into the extract and then an aliquot was measured using GC-MS.

Each sample was analyzed on an Agilent 7890 GC equipped with a 51-m DB-5MS column (0.25 µm film thickness and 0.25 mm inner diameter) and detected on a 5890C mass spectrometer (Agilent, Santa Clara, CA, USA). Each analysis by GC-MS had a heating ramp of 40 °C for 1 min, ramped to 80 °C at 40 °C/min and then ramped to 320 °C at 25 °C/min and held for 5 minutes. The split/splittless injector was kept at 300 °C and had a split ratio of 10:1. The GC method had a He flow rate of 0.6 mL/min with a solvent delay of 4.50 min. The MS had a m/z range of 33-550.

III.7 TD-Py-GC-MS

TD-Py-GC-MS was performed using a CDS Analytical, Inc (Oxford, PA, USA) 5000 series pyroprobe (run in trap mode with a Tenax-TA^{TM} trap sorbent) connected by a transfer line to an Agilent GC 7890 equipped with a 51-m HP-5MS column (0.25 µm film thickness and 0.25 mm inner diameter) and detected by an Agilent 5890C mass spectrometer.

Quartz wool was placed inside a quartz tube (CDS Analytical, Inc., Oxford, PA, USA) which was used on the pyroprobe. Prior to the experiment, the tube with quartz wool was cleaned outside of the probe at 1200 °C for 5 s then allowed to cool before sample introduction.

An aliquot (500 µL) from each sample from the hydrotreatment experiments was analyzed, 5 µL IS (10,000 ppm o-terphenyl) was added. Samples were vortexed for 10 seconds before a 5 µL aliquot was spiked. The probe was then immediately inserted into

the assembly and dried at 50 °C for 60 seconds. The probe then heated at 10 °C/s to the desired temperature where it was held isothermally for 30 s. The transfer line and valve oven were kept at 300 and 320 °C, respectively. The assembly was held at 300 °C for 2.5 minutes while the trap was kept at 45 °C to trap eluting compounds before heating and holding 300 °C for 3 minutes. Each sample was subjected to sequential fractional heating of 200, 300, 400, 500 and 870 °C where each fraction was first collected on the trap and then transferred to the GC/MS analyzed using the same method as above.

CHAPTER IV

RESULTS

IV.1 TCA Optimization

Sample Introduction

First, the impacts of solvent and sorbent used for sample introduction were studied, evaluating the losses by vaporization during the drying step for H_2O, MeOH and DCM with syringol as a dissolved analyte.

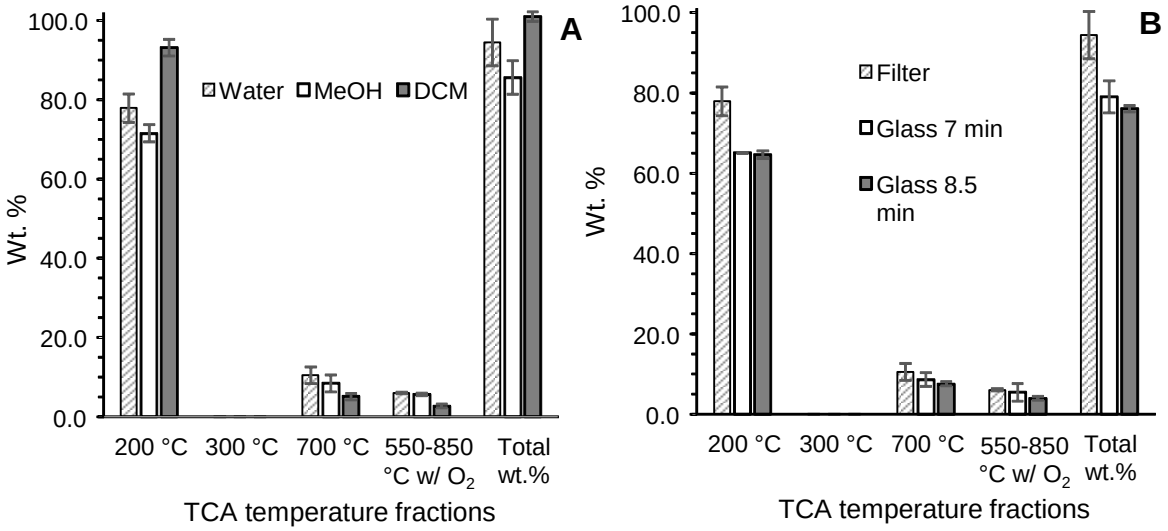


Figure 5. TCA thermal profiles of syringol (7 µg) used as a model compound A) in three different solvents; H_2O, MeOH and DCM, the drying of 7 min for water and 4 min for MeOH and DCM at 40 °C prior to the analysis and B) In H_2O spiked onto a quartz filter surface and glass surface while changing the drying time prior to analysis.

The TCA profiles were similar for all three solvents (Fig. 5a) and loading surfaces (Fig. 5b). When water and DCM were used as solvents for syringol, there was near 100 wt. % recovery. However, when MeOH was used, there appeared to be a small loss potentially due to co-vaporization. The bulk of syringol evolved during the first 200 °C temperature step. Unexpectedly, a small portion of carbon, 6 wt. %, evolved as a coked fraction in the

presence in oxygen. It is of note that this fraction is usually not accounted for during analysis of lignin and its degraded products. For DCM, the fraction evolving at 200 °C was slightly greater than for the other solvents. A slight difference was observed in the TCA thermal profiles between the quartz filter and glass surface with changing drying times. While the quartz filter with water had about 100 wt. % recovery, there appeared to be a loss when using the glass boat without the filter. This loss could be due to volatilization of the sample which adheres to the quartz filter. The quartz filter was used for all subsequent experiments due to its larger loading capacity and shorter drying time.

Reduction of Pyrolytic Fraction

In the experiment described above we have demonstrated that a fraction of some compounds, including even small MW aromatics, evolved as either pyrolyzed or coked carbon, i.e., either in the fraction that evolves at 700 °C (pyrolyzed) or the fraction that evolves at greater than 700 °C with the addition of oxygen (coked). We have aimed our optimization of conditions to minimize both the pyrolyzed and coked fractions. This was based on the hypothesis that if the compounds were evolved at low temperatures, the fraction of pyrolyzed/coked carbon would be lower. Thermal TCA profiles of varying the initial step for guaiacol, syringol, vanillin, levoglucosan and pinoresinol can be seen in Appendix VI.

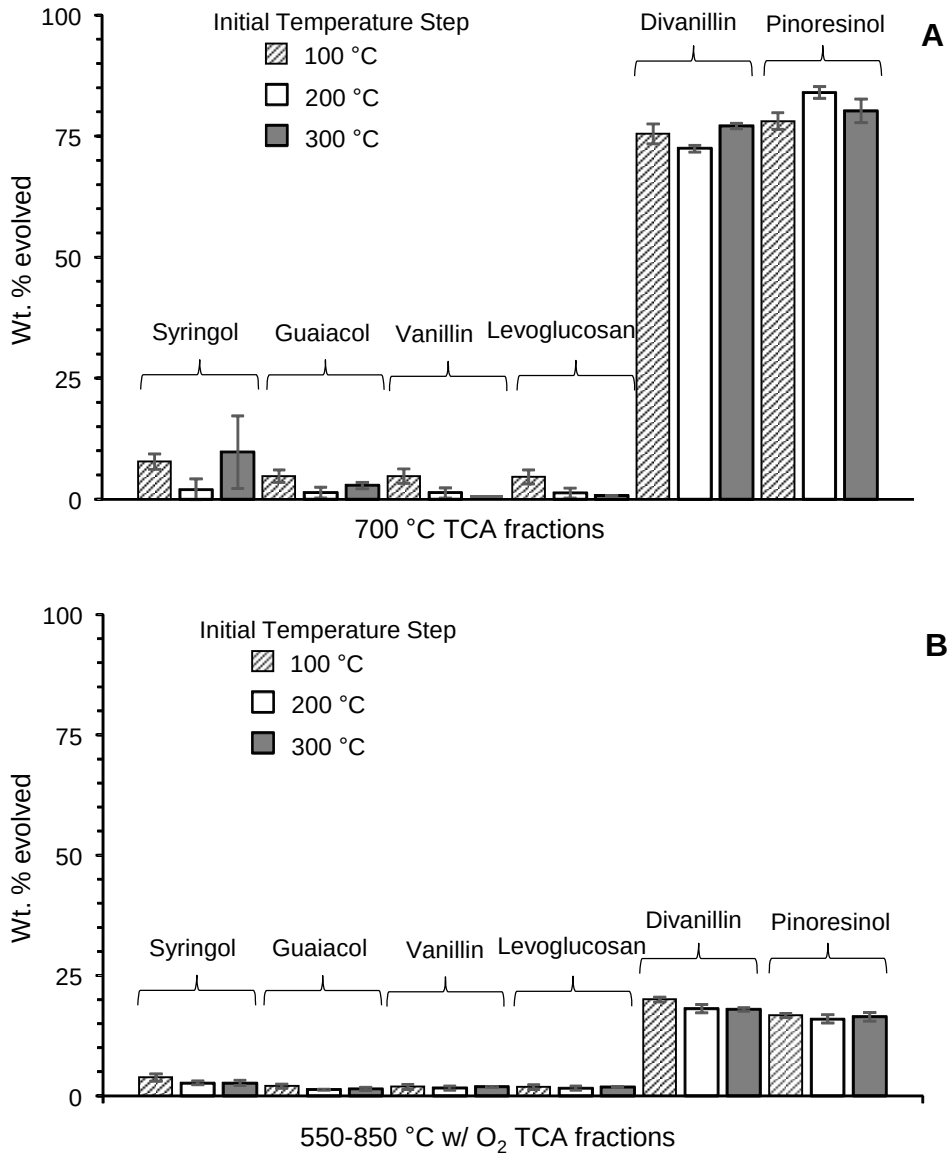


Figure 6. Comparison of the pyrolytic fraction of carbon (A) and the amount of coked carbon (B) due to variation of TCA initial temperature step.

There appeared to be a trend in the high temperature fraction without oxygen (Fig. 6A) that a higher wt. % of carbon is evolved when the initial temperature step was 100 °C. Contrary to our expectations, the coked fractions did not differ whether the programming started with 100, 200 or 300 °C for any of the mono- or di-aromatic compounds evaluated (Fig. 6B). However, this could be due to not all of the analyte evolving at low temperatures thus requiring higher temperatures for complete evolution. This hypothesis could be

explored by including an additional sequential step after the initial 100 °C before the 700 °C fraction, e.g., 100, 200, 700 and 550 – 850 °C, however this was not investigated yet as the differences were only several %.

It should also be noted that the amounts of the coked fraction from analytes with high boiling points, pinoresinol and divanillin, were much higher than those of smaller size monomeric standards. This observation indicates that the interactions of adsorbed molecules with the active sites on the quartz filter may be so strong that desorption temperature from this sites results in covalent bonds breaking at lower temperatures before the weaker sorbate-sorbent interactions are broken. Apparently, this effect is more pronounced for larger molecules with multiple functional groups forming multiple interactions with the adsorbent, which are unlikely to break simultaneously.

It was concluded that changing the initial temperature step did not have any significant effects on the amount of pyrolyzed/coked carbon. Henceforth, experiments including fractional temperature steps will start at 200 °C. This avoids incomplete evolution by analytes from starting at 100 °C, while still being low enough to start characterizing low molecular weight species from lignin degradation products.

Loading Volume

The amount of sample spiked onto the quartz filter was evaluated. Unlike the previous optimization studies, this study used samples produced from the hydrothermal treatment as opposed to standards. Fig. 7A shows the linearity of increasing the sample amount spiked onto the filter and total integrated mass of carbon detected based on a sucrose calibration (Appendix I & II).

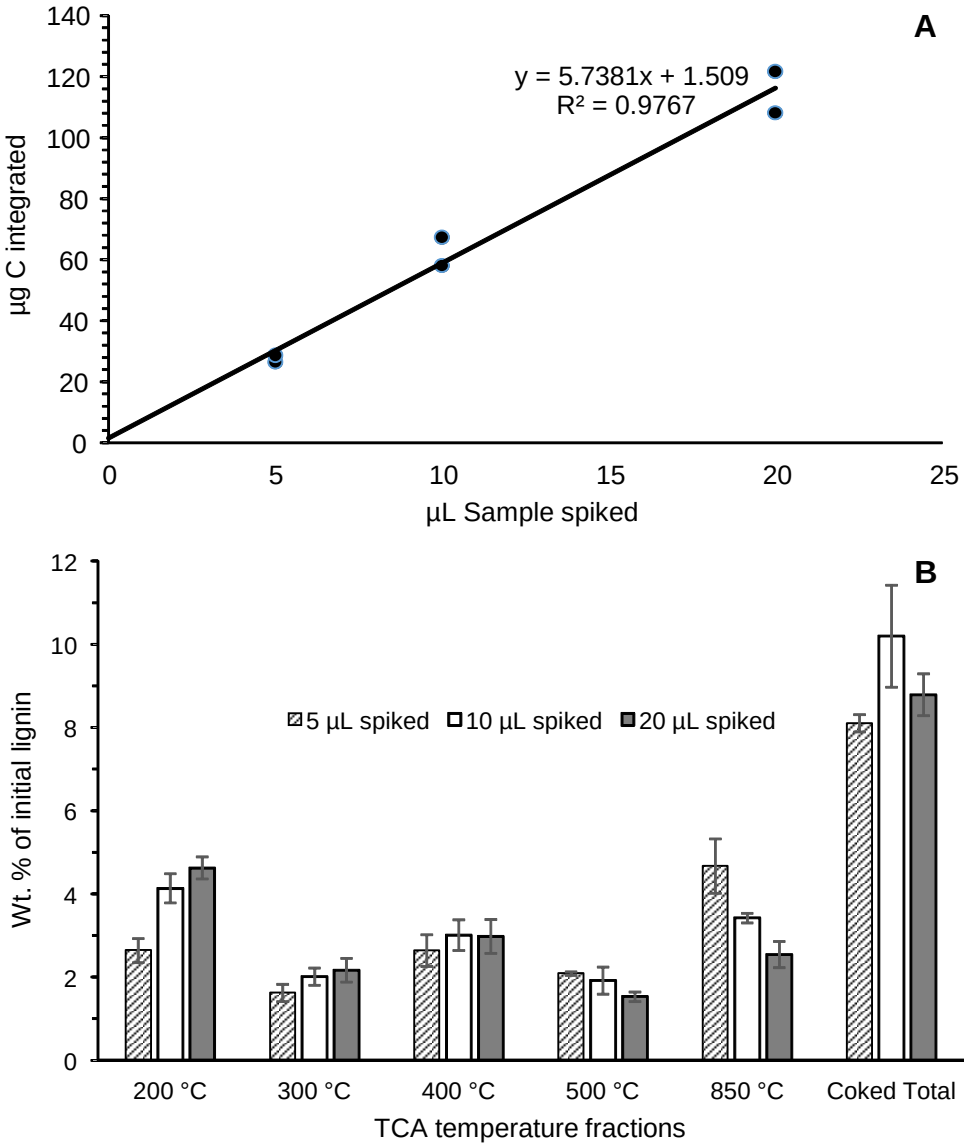


Figure 7. Varying loading amounts evaluated using TCA. A) The linearity of response with increasing loading amounts. B) Thermal profiles of different sample loading volumes.

Figure 7B shows the thermal profiles of the same sample with different loading amounts. Unexpectedly, the responses across the temperature fractions appear to differ from each other. This was particularly apparent for the 200 and 850 °C fractions namely as the sample volume increased, the wt. % for the 200 °C fraction also increased while the opposite was true for the 850 °C fraction. This trend appears to be due to analyte retention

caused by non-specific strong analyte adsorption on the surface of the quartz filter. This adsorption occurs only on a few sites which is why there is a greater effect with lower loading amounts. When a small amount of sample is loaded, the saturated active sites bind to the analytes and release the analytes at a higher temperature.

IV.2 TCA Application to Lignin

Evaluation of Lignin TCA Temperature Profiles

To ensure the method applicability to both lignin and its degradation products (both high and low MW compounds), we performed a further evaluation of thermal TCA profiles using untreated alkali lignin, for which multistep heating was essential (Fig. 8).

Initial experiments involved heating lignin in sequential temperature steps of 50 °C increments. Originally each temperature step was held for 1 minute but this made it difficult to distinguish between different temperature fractions as the fractions co-eluted with each other. To better resolve the fractions, the isothermal zones were held for 5 minutes each (Fig. 8A).

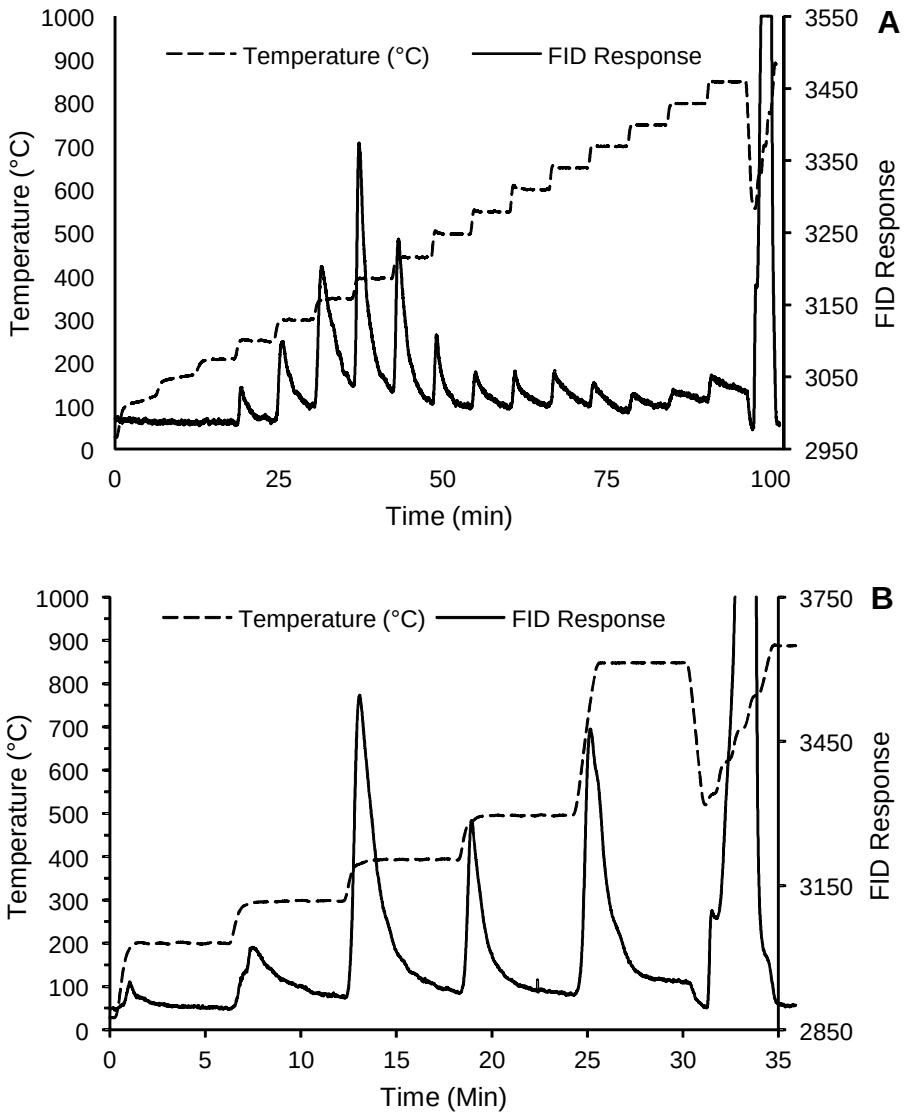


Figure 8. TCA thermograms of alkali kraft lignin with an overlaid temperature program. A) Each temperature step was set up as by 50 °C starting at 100 °C and held for 5 min. B) Each temperature step was increased by 100 °C starting at 200 °C and held for 5 min.

The use of 50 °C increments displayed that lignin evolved the most at 400 °C. With the large number of temperature steps, each being held for 5 minutes, the analysis time per sample was lengthy, which would result in a slow throughput of samples. To still achieve a comprehensive analysis of lignin and its degradation products and to ensure feasibility, we reduced the temperature steps starting with thermal desorption at 200 and 300 °C for the low MW fraction (GC-elutable monomers and dimers), followed by 400, 500, and 870

°C steps evolving high-MW pyrolyzed fractions, and the final step of 890 °C with the addition of O_2 to evolve any coked product. 200 °C was also included to compare thermal profiles to that of untreated lignin. This TCA program was employed for characterization of alkali lignin. Since the method was aimed at the characterization of lignin degradation products produced by hydrotreatment, we compared the TCA profile of dry lignin to that of lignin suspended in pure water. These two experiments showed similar results (Fig. 9). A significant benefit of introduction of lignin as an aqueous suspension is elimination of the necessity of weighing small amounts i.e., µg, which requires a high accuracy microbalance. In our method we have accounted for 94.8 ± 5.5 wt% of all carbon (present in initial lignin) in the suspension. We have noted that aliquots of the suspension must be taken during sample mixing to ensure sample homogeneity.

The results confirmed that lignin starts to thermally decompose at relatively low temperatures of 200 – 275 °C.[9] The majority of lignin-derived products evolved at 400 °C similarly as reported for TGA.[39] Nevertheless some of the lignin continued to evolve at higher, pyrolytic temperatures (850 °C). A notably significant portion was observed in the "coked" fraction being evolved only in presence of oxygen (seen as the last peak) corresponding to greater than 50 wt% in Fig. 8 and is quantified in Fig. 9.

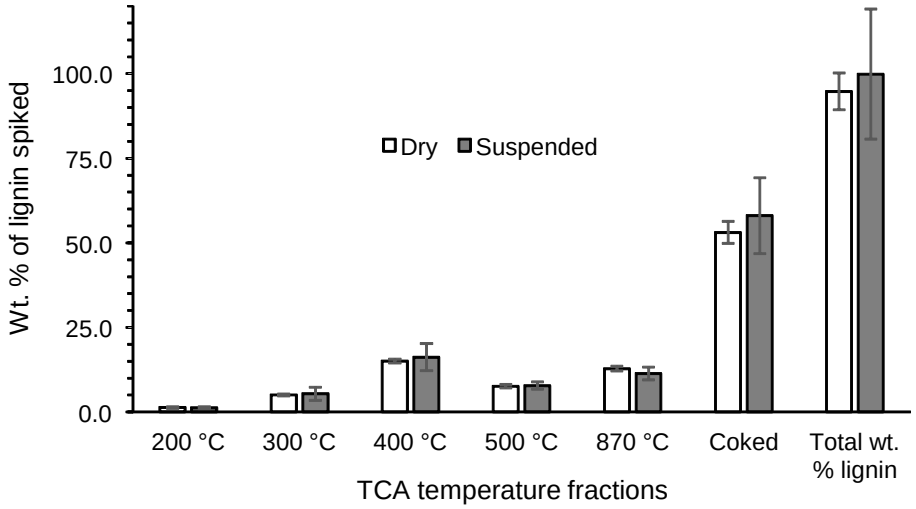


Figure 9. Thermal TCA profile of alkali lignin introduce dried and as aqueous suspension in water and raw lignin.

It should be noted that for both dry and aqueous samples, 100 % mass balance was achieved. This also supported by no significant differences in the thermal profiles between the dry lignin sample and lignin that was suspended in water. Suspended samples that were dispensed had less precision in their thermal profile fractions. This could be due to the method of spiking onto the quartz filter. For the dry sample, lignin was placed onto the filter directly and then weighed with a microbalance. The liquid samples were transferred using an automatic pipette which would often have adhesion of lignin particles either on the inside or outside of the tip. Samples from hydrothermal treatment experiments were spiked onto the TCA using automatic pipettes as a microbalance was not readily available.

TCA vs TGA

Validation of the TCA method was conducted by analysis of alkali lignin on TGA with a similar multistep heat ramp, in which each temperature was held for 5 minutes. Major differences between thermal techniques is that TGA is based on gravitational measurements while TCA is selective only for carbon. Differences between the methods

are shown in Table 1 and Fig. 10. The TCA method uses much less sample and is able to achieve a higher and more controlled heating rate. When a higher heat ramp (100 °C min^{-1}) was used with the TGA, the sample temperature significantly exceeded the target temperature resulting in an inaccurate temperature ramp. Analysis by TGA not only took longer due to heating rate but also the cool down time was lengthy, taking an additional 45 minutes whereas cool down time with TCA was less than 5 minutes.

Table 1. Differences in methods between the analysis of alkali lignin with TCA and TGA.

	Mass Loaded (mg)	**Heat Ramp (°C min^{-1})**
TCA	0.050	300
TGA	20	25

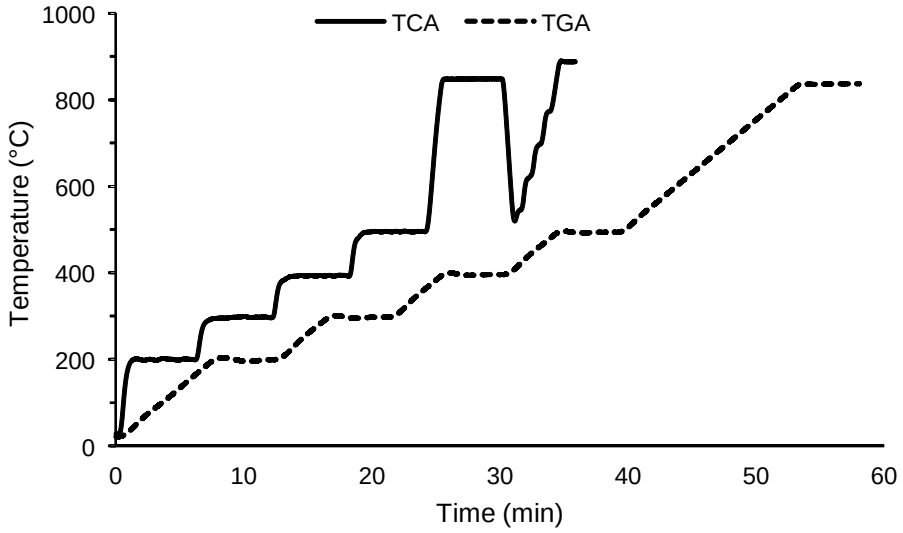


Figure 10. Comparison of temperature programs between the TCA method and TGA method.

Similar to the thermogram from the TCA, a thermogram was derived from TGA by plotting the change in wt. % vs. time (Fig. 11A). The thermogram derived from the TGA analysis has an extra peak at the start of the experiment, which is caused by moisture loss

and is equivalent to the amount of moisture determined in lignin previously, see Appendix VII.

The coked fraction seen in Fig. 11 was determined on the TCA as the mass evolving with the addition of oxygen while the coked fraction on the TCA was determined by the remaining fraction after analysis.

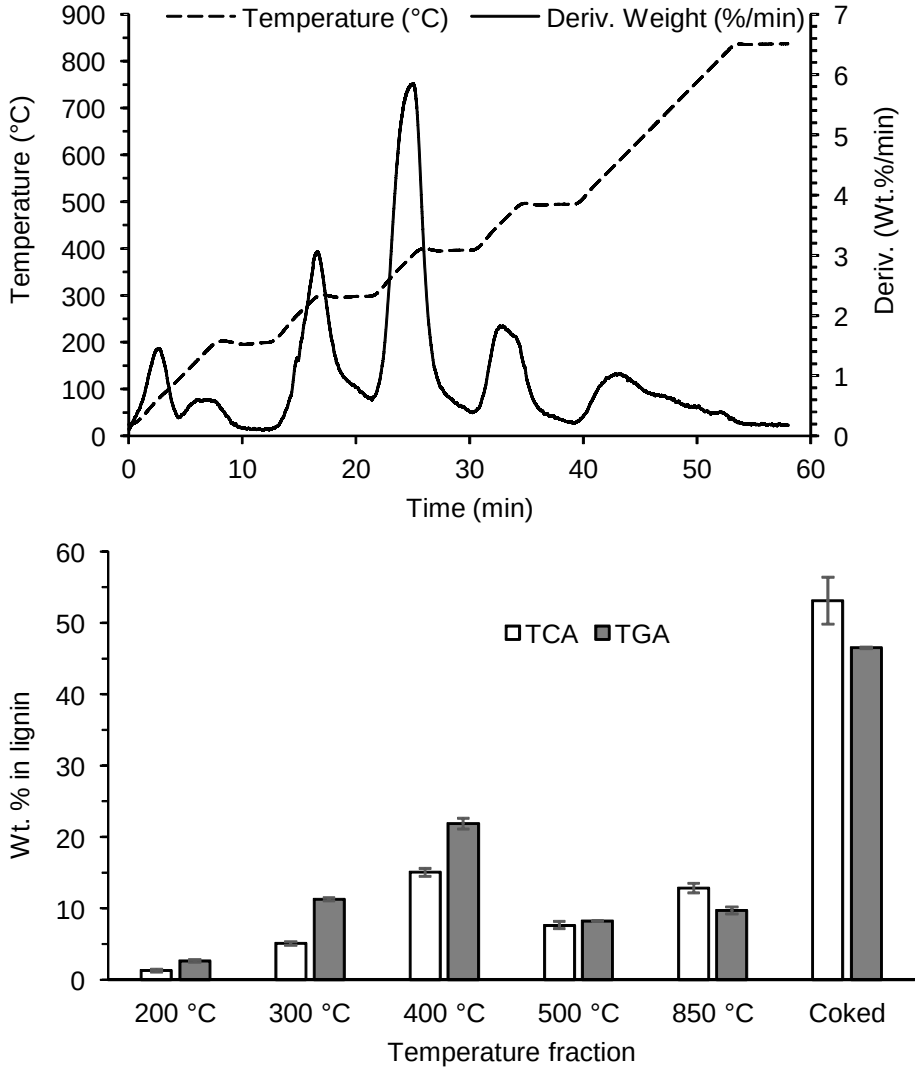


Figure 11. A) Derived TGA thermogram of lignin B) Comparison of lignin analyzed via TCA and TGA. The TCA and TGA used ~0.050 mg with a heat ramp of 300 °C min $^{-1}$ and ~20 mg with a heat ramp of 25 °C min $^{-1}$, respectively.

The thermal profiles of kraft lignin are similar between TCA and TGA, which is apparent at higher temperatures. TGA validates the TCA method but also shows advantages of using TCA. There are slight differences in the lower temperature fractions. First, TCA is selective for carbon only where as TGA which could be measuring any inorganic losses up to 400 °C from improper isolation of lignin from biomass or adhesion of water. The second reason for greater abundance at lower temperatures with TGA is that oxygen is not accounted for by the TGA, which amounts to 10 - 15% of the MW of oxygenated species. The TCA method shows a higher amount of coking, which could be due to lower spiking amounts than TGA as discussed previously. TCA allows for low sample loading and faster heating ramps vs the TGA method.

TD-Py-GC-MS of Lignin

Lignin was analyzed using the same temperature program as employed for the TCA method with the goal to identify specific products in each temperature fraction, complementing the TCA. The products identified are described in detail in the text below and shown in Table 2. The most abundant products identified were methoxyphenols: guaiacol and vinylguaiacol along with a mixture of other guaiacol derivatives, with the exception of higher temperatures producing a significant amount of phenolics.

As for the TCA (Fig. 9), very few compounds evolved within the initial 200 °C TD-Py-GC-MS fraction. Also similar to TCA, a significant elution was observed as the temperature increased from 200 to 300 °C. By contrast, the fraction evolving at 400 °C did not exhibit a trend similar to TCA, showing only very few species. The 500 °C fraction showed the highest abundance of organic species.

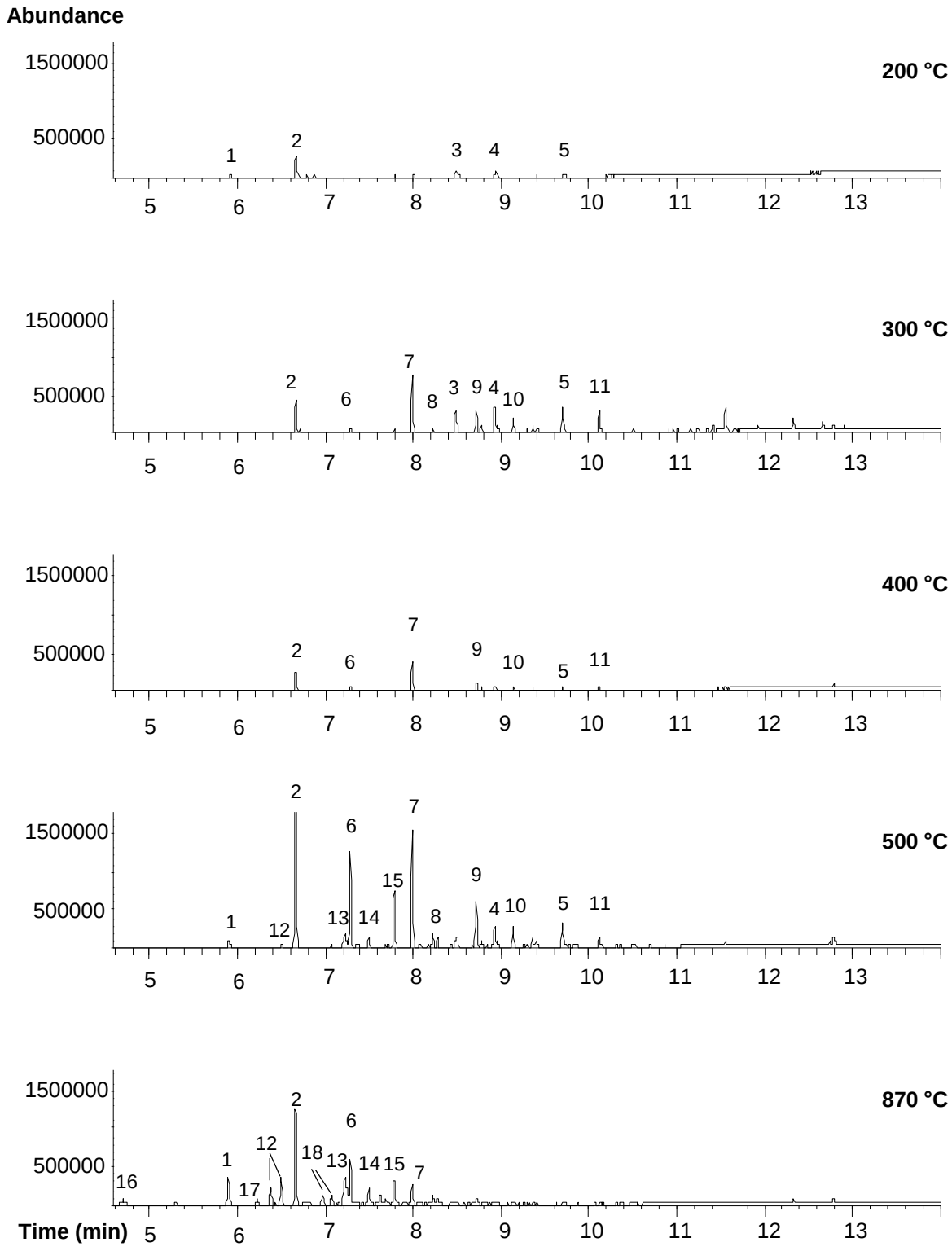


Figure 12. Fractional TD-Py-GC-MS of lignin, products identified can be seen in Table 2.

The difference in thermal profiles when comparing TCA and TD-Py-GC-MS could be explained by the evolution of gases from lignin degradation. CO, CO_2, and CH_4 are known to be formed during lignin pyrolysis at temperatures as low as 230 °C and increasing in formation up to 500 °C.[9] Production of CO, CO_2 and CH_4 can be a result of the dissociation of diarylether bonds, weakly bonded methoxy groups and carboxyl groups.[9, 46] It is also possible that CO_2 is formed as a product of combustion with the oxygen naturally available in lignin. This evolution of gases would be detected during the TCA analysis as they are formed during the quantitative conversion of products into CH_4 while they are not seen during the analysis with TD-Py-GC-MS, as the Tenax-TA trap on the pyroprobe would not retain them. Nevertheless, it can be concluded that TD-Py-GC-MS is a complementary method to the overall characterization of the thermal degradation of lignin.

IV.3 TCA Application to Hydrotreated Samples

Product Distributions with Changing Hydrotreatment Temperatures

Alkali kraft lignin was hydrothermally treated in the analytical static batch reactor seen in Fig. 4 with the goal to produce potential high value chemicals. To assess repeatability, replicates of 5 vessels were prepared with only lignin and water. The samples were heated to multiple temperatures ranging between 200 and 300 °C as seen in Fig. 13 and held at the desired temperature for at least 15 minutes after the vessels reached the oven temperature. Appendix V gives heating curves of the vessel vs. oven temperatures.

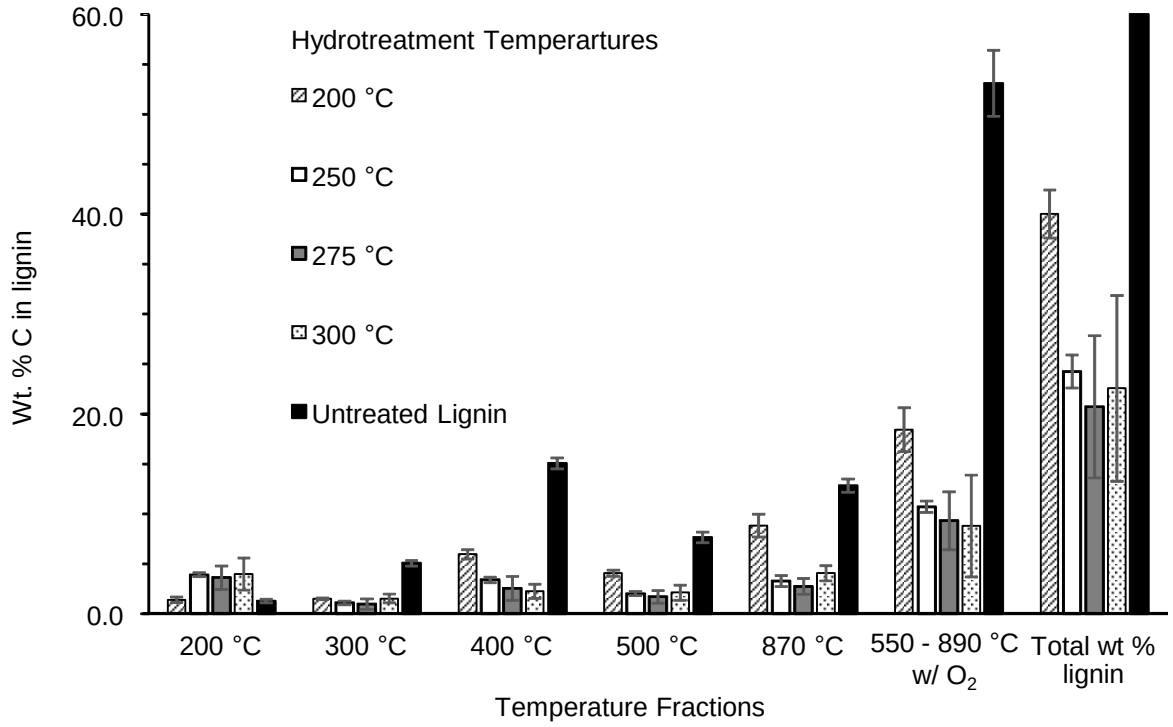


Figure 13. Thermal profile distribution of products from hydrothermal treatment at varying reaction temperatures, untreated lignin was lignin suspended in water at room temperature.

The use of sequential temperature fractions using the TCA method provided insight into the chemical characterization of lignin decomposition products. As the hydrotreatment temperature increased, there is was an increase in the fractions at 200 °C, i.e., phenolic monomers. Keeping this in mind, other temperature fractions can be assigned qualitatively to higher-MW oligomers because larger MW species require a higher temperature to evolve. Products evolving between 300 – 400 °C were classified as dimers and trimers formed from lignin degradation. However, these may also be gases forming as discussed above, which are detected with TCA as the method is selective for carbon but is independent of carbon speciation. It is hard to interpret the quantity of these gases in this fraction as the TD-Py-GC-MS is only semi-quantitative. Products evolving at 500 °C may represent larger oligomers, and the products at 850 °C fraction reflect any remaining

undegraded lignin that is still able to be treated. This treated able lignin may be a result of remaining initial lignin or also a product of repolymerization from lower MW species.

Interestingly, we have shown for untreated lignin a low abundance fraction evolving at 200 °C, which may be due to unbound impurities capsulated within lignin. As lignin was hydrotreated at higher temperatures, an increase in monomer formation from 200 to 250 °C was observed; however, there was no significant change from 250 to 300 °C. This feature may be explained by the abundant fraction at 870 °C, that was unexpected. This fraction may be formed due to repolymerization of lignin degradation products occurring when treated at 300 °C. It has been reported in recent literature that the yield of monomers produced from subcritical water treatment reaches a maximum at a certain time, after which it declines due to severe repolymerization reactions.[11, 18]

The total wt. % recoveries for the hydrotreated samples were substantially lower than that of untreated lignin suspended in water (100 ± 19 wt. %). The large variation may be due to adhesion effects to the pipette tips as mentioned before. The low mass recovery of hydrotreated samples may be due to the high amount of residual product that remained in the vessel even after thorough rinsing.

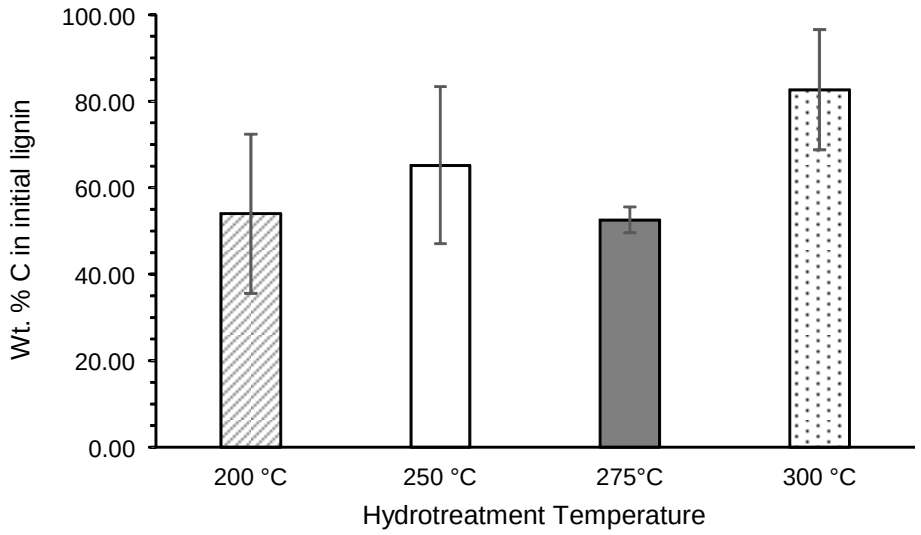


Figure 14. Wt. % of solid residue found in the reaction vessels after hydrothermal treatment.

The total residue seen in Fig. 14 shows a correlation of the total wt. % recovered by analysis with the TCA results shown in Fig. 13. The mass balances near recovery were seen in the 200, 250 and 300 °C samples. For example, during the 300 °C hydrotreatment, 82 ± 14 wt. % remained in the vessel while the total wt. % from TCA was 23 ± 9 %. As seen in Fig. 14, there was a decrease in total wt. % recovered while the temperature increases, which is opposite to what is seen in Fig. 13. It is difficult to interpret the trend of increasing residue remaining in the vessels with higher temperature due to the large deviations, however it could be caused by more tar formation on the vessel walls due to elevated temperatures. Regardless, the relationship between the TCA recovery and the vessel residue was still reassuring as it provides a satisfactory overall mass balance closure, e.g., the total wt.% recovered by TCA and remaining residue from vessels of lignin hydrotreated at 300 °C is about 20 and 80 wt. %, respectively.

TCA vs LLE GC-MS

Liquid-liquid extraction (LLE) with GC-MS is a conventional method for analyzing products from hydrothermal treatment is to isolate the analytes from an aqueous phase to an organic phase.[14, 47] Since analysis by GC requires the products to be volatile and due to heat restrictions by conventional GC ovens, the assumption is made that products evolving from the 200 and 300 °C fractions by TCA are also GC-elutable. Thus comparison of LLE - GC-MS analysis and the GC-elutable fractions from TCA data was pursued to confirm this assumption, further more GC-MS analysis is aimed to provide identification of species present in low temperature fractions.

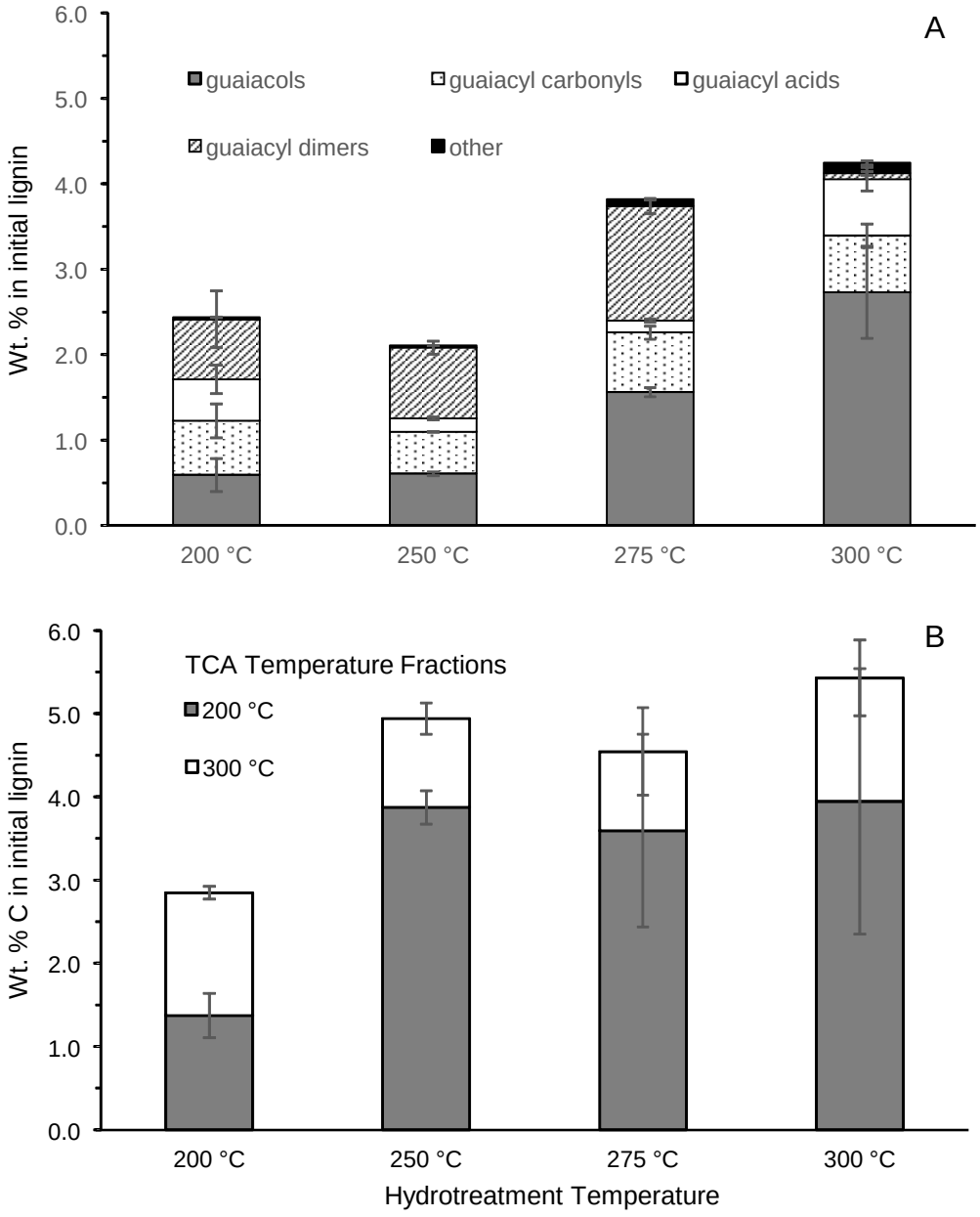


Figure 15. A) Summary of product composition from hydrothermal treatment experiments prepared by LLE with DCM followed by analysis with GC-MS. B) TCA analysis of the same samples before LLE was performed, only the 200 and 300 °C are shown.

The assumption that the 200 and 300 °C fractions from TCA are GC-elutable products is supported in Fig. 15, individual species quantified in Fig. 15A are detailed in Appendix VIII. There is a strong correspondence between the total wt. % extrapolated from the GC-MS and TCA analysis. Although the total wt. % values from each analysis are similar, it should be noted that the overall wt. % values from the 200 and 300 °C TCA

fractions are slightly higher than the respective total wt. % for each hydrothermal treatment temperature.

Differences between LLE-GC-MS and TCA could be due to the following factors. One possibility is that not all of the analytes that are GC-elutable were fully extracted due to the partitioning of analytes being governed by polarity or functional group interactions with the organic solvent.[47] For example, there could be polar analytes that are not soluble in relatively nonpolar dichloromethane.

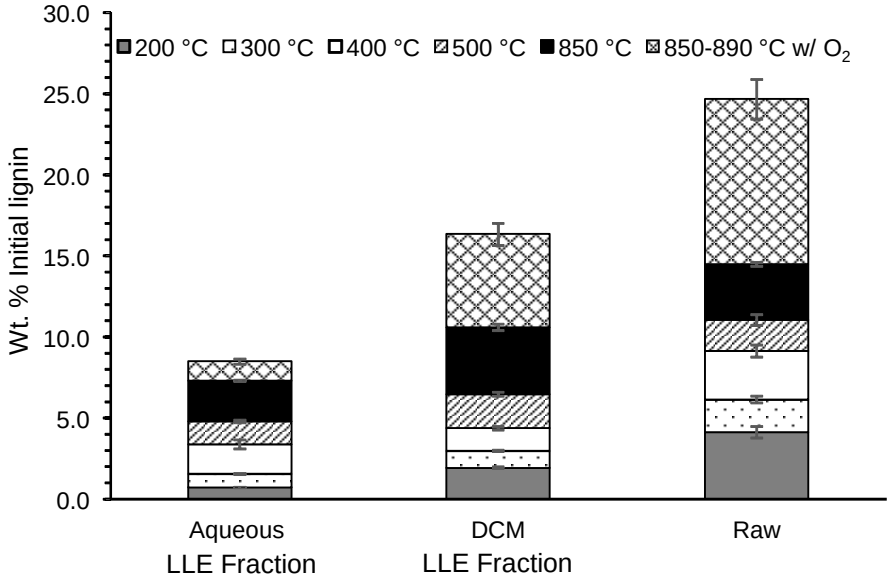


Figure 16. LLE fractions of 300 °C hydrotreated samples analyzed on TCA. "Raw" refers to the sample directly out of the vessel, DCM is the extracted fraction and aqueous is the water remaining after extraction.

To evaluate the extraction efficiency further, fractions from different stages of the extraction were analyzed by TCA. As seen in Fig. 16, not all of the GC-elutable products are extracted into the DCM phase. The sum of the total wt. % recovery for the aqueous phase and DCM are equivalent to the total wt. % of the sample before extraction indicating no sample loss during extraction. The results show that there is about 1.5 wt. % in the

aqueous phase that could be GC-elutable being from the 200 and 300 °C fractions, which correlates with the product evolving on the TCA as shown in Fig 15B.

Another possible interference for the observed difference in TCA and GC profiles could be strong interactions with the stationary phase of the GC column. Although an analyte may be volatile enough to evolve below 300 °C on the TCA, it is not guaranteed to pass through the nonpolar GC column. Acids, for example, hydrogen bonding that is stronger than the combined induced dipole-induced dipole and dispersion forces of the C_{18} stationary phase. This may result in little to no acids passing through the column. Lastly, common products from lignin decomposition, CO and CO_2, have been reported to form at temperatures as low as 200 °C.[9, 41, 48] It is possible that these gases are formed from higher MW compounds during the TCA analysis and could cause discrepancies with the GC-MS analysis as it is not accounted for.

TD-Py-GC-MS of Hydrotreatment Products

To further evaluate both methods, the results form TCA and TD-Py-GC-MS were compared for the products of lignin hydrothermal treatment. The products were identified based on a mass spectra match greater than 75% from the NIST Standard Reference Database 1A. Table 2 summarizes the products found, which were numbered based on their appearance with increasing the hydrothermal treatment and pyrolysis temperatures, i.e., products that appeared as a result of higher hydrothermal treatment temperatures have higher peak numbers.

Table 2. List of products tentatively identified from the analysis of hydrothermal treated using TD-Py-GC-MS including retention times, specific MS, the corresponding peak numbers were used in Figs. 12, 17-21.

Peak Number	Ret. Time (min)	Compound Name	Major Ions	Compound Class
1	5.92	Phenol	94, 66, 39	Phenols
2	6.68	Guaiacol	109, 124, 81	Guaiacols
3	8.5	Vanillin	151, 152, 81	Guaiacyl carbonyls
4	8.94	Acetovanillone	151, 166, 123	Guaiacols
5	9.71	Vanillic Acid	137, 182, 207	Guaiacyl Acid
6	7.3	Methylguaiacol	138, 123, 95	Guaiacols
7	7.99	Vinylguaiacol	150, 135, 107	Guaiacols
8	8.22	Eugenol	164, 144, 103	Guaiacols
9	8.72	Isoeugenol	164, 149, 131	Guaiacols
10	9.14	Homovanillyl alcohol	137, 180, 122	Guaiacyl Alcohols
11	10.13	4-Hydroxy-2-methoxycinnamaldehyde	178, 161, 197	Gauaicyl Carbonyls
12	6.5	Methylphenol	107, 108, 77	Phenols
13	7.23	Catechol	110, 64, 81	Phenols
14	7.5	Dimethoxytoluene	152, 137, 109	Phenols
15	7.78	Ethylguaiacol	137, 152, 122	Guaiacols
16	4.69	Toluene	91, 92, 65	Phenols
17	6.22	4-Methylanisole	122, 121, 77	Phenols
18	7	Dimethylphenol	107, 122, 121	Phenols
19	7.63	3-Methylcatechol	124, 123, 78	Phenols
20	8.78	Propylguaiacol	137, 166, 122	Guaiacols
21	8.18	Syringol	154, 139, 96	Guaiacols
22	8.41	2-Methoxy-1,4-benzenediol	140, 125, 97	Guaiacyl Alcohols
23	7.07	Ethylphenol	107, 122, 77	Phenols
24	6.95	Dimethoxybenzene	138, 95, 123	Phenols
25	5.3	Xylene	91, 106, 105	Phenols
26	6.67	Methoxyphenol	109, 124, 81	Phenols

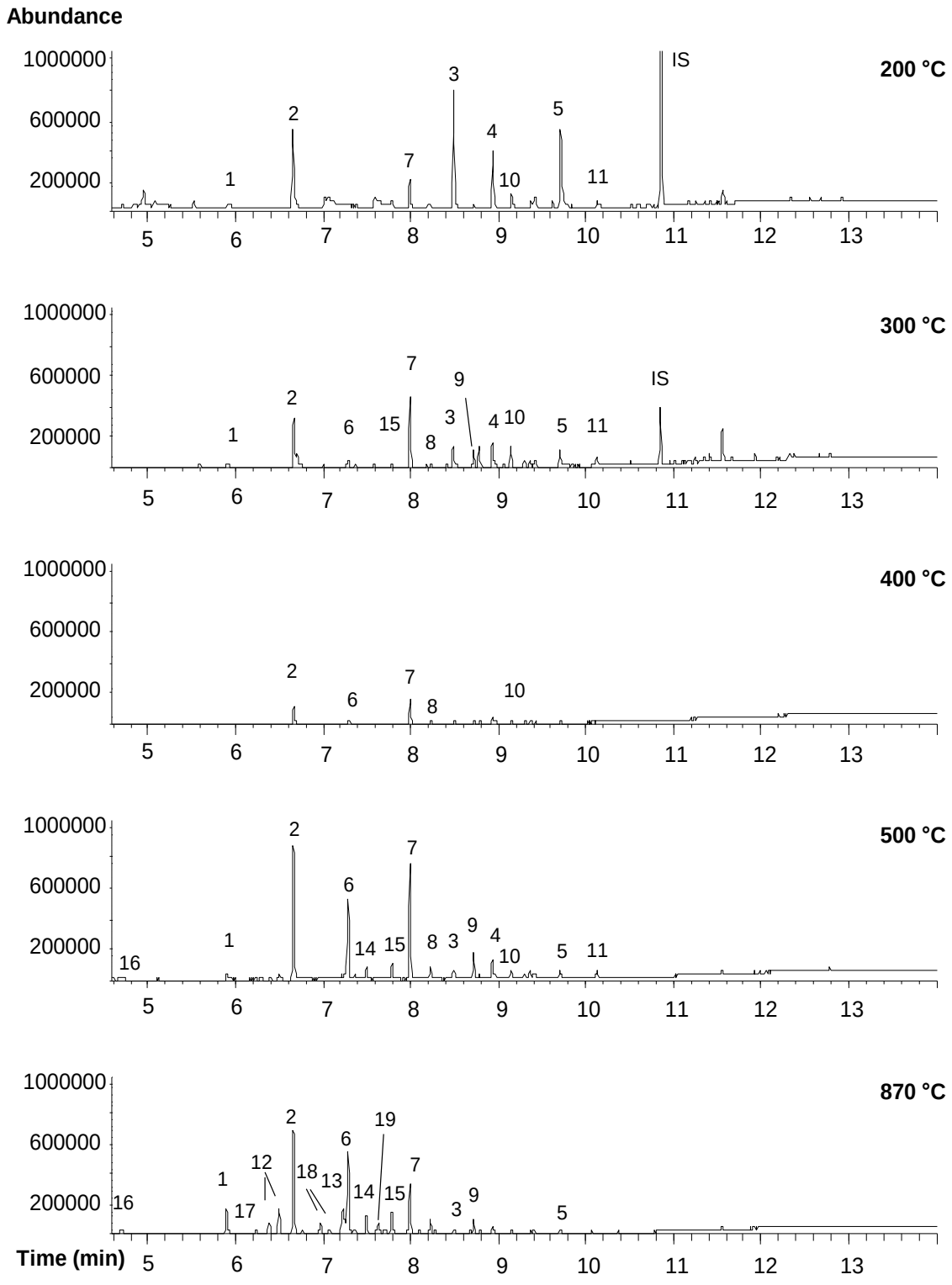


Figure 17. Fractional TD-Py-GC-MS analysis of lignin hydrotreated at 200 °C, the peak numbering corresponds to the products identified in Table 2.

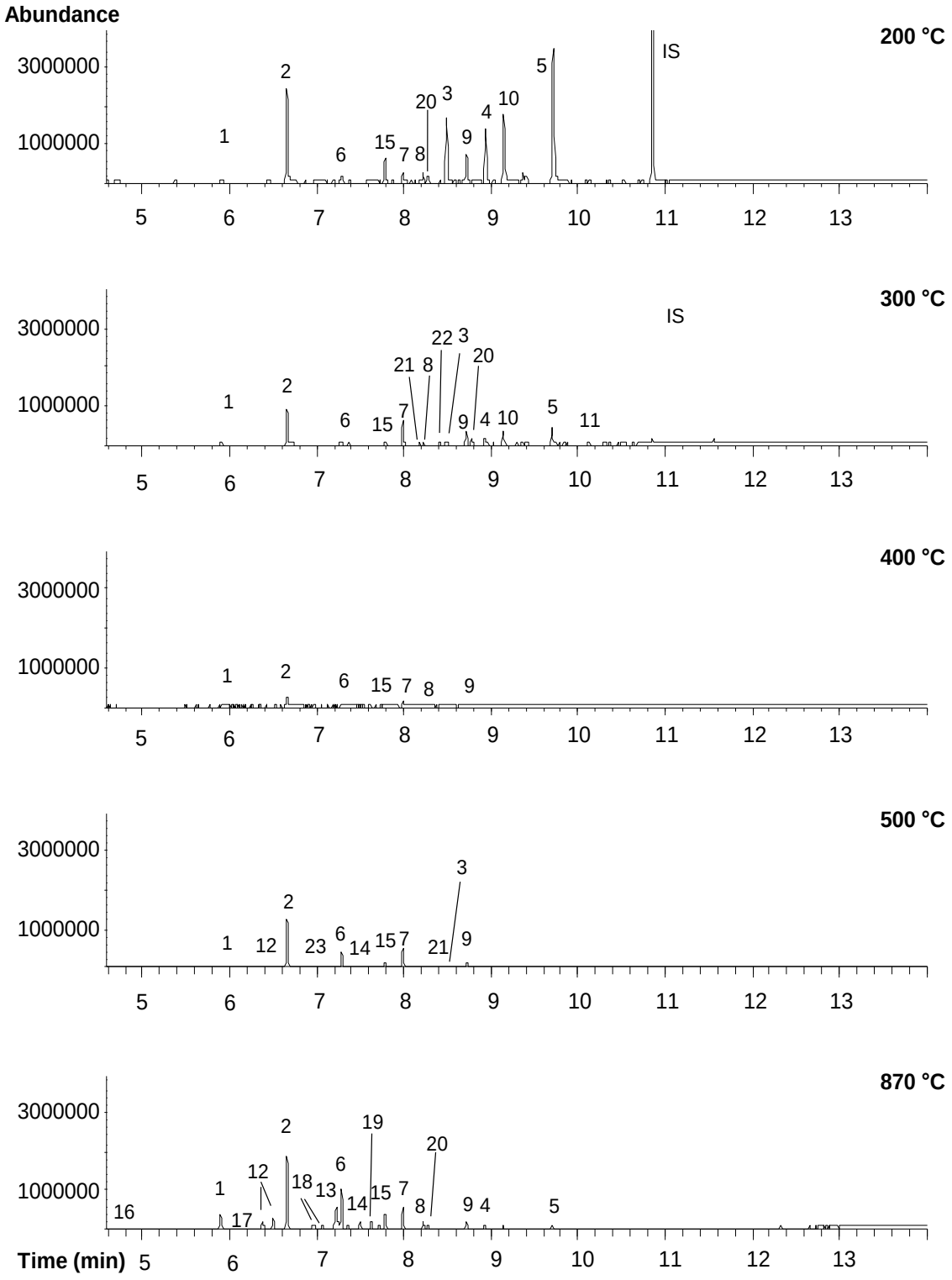


Figure 18. Fractional TD-Py-GC-MS analysis of lignin hydrotreated at 250 °C, the peak numbering corresponds to the products identified in Table 2.

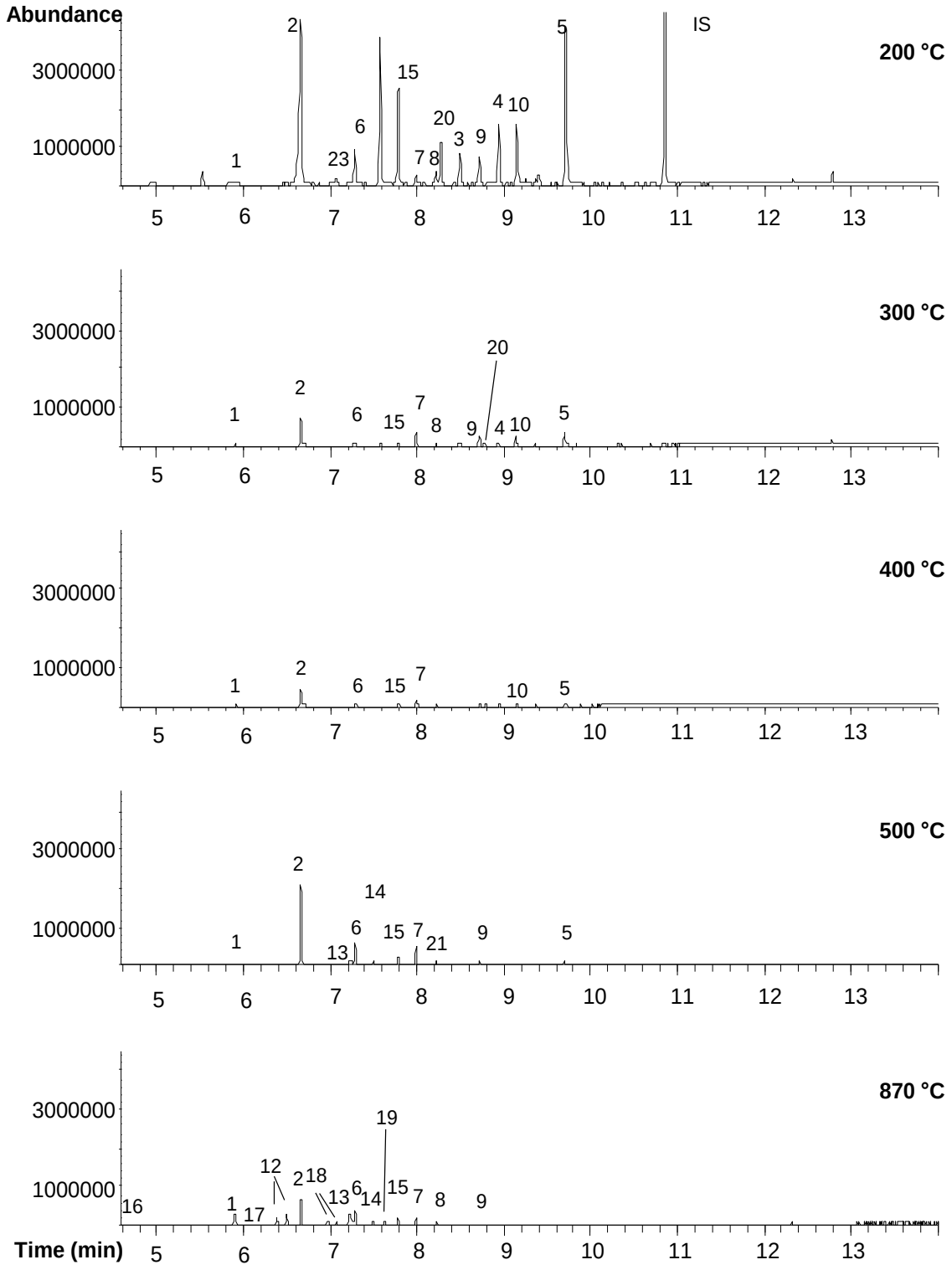


Figure 19. Fractional TD-Py-GC-MS analysis of lignin hydrotreated at 275°C, the peak numbering corresponds to the products identified in Table 2.

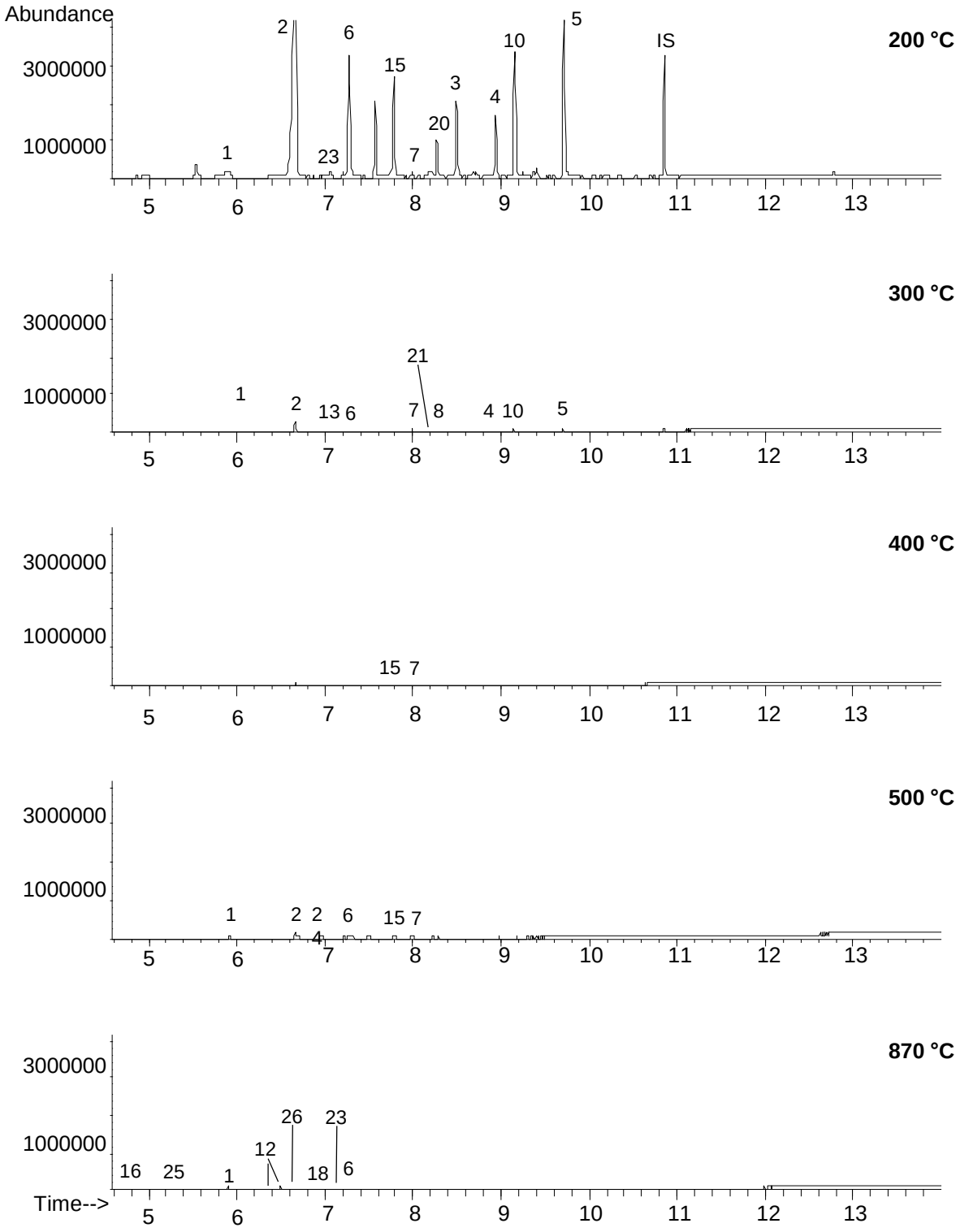


Figure 20. Fractional TD-Py-GC-MS analysis of lignin hydrotreated at 300 °C, the peak numbering corresponds to the products identified in Table 2.

For the hydrothermal lignin treatment products, the majority of observed species were guaiacyl derivatives. At lower (TD) temperatures methoxy aromatic compounds were found in higher amounts while at higher (pyrolysis) temperatures, a large abundance of benzene and phenolic products was detected, which could be a result of side reactions (demethoxylation or demethylation).[49] It could also be a result of the decomposition of either oligomeric products from hydrothermal treatment or even unreacted lignin.

Similarities were seen between thermal desorption fractions (200 and 300 °C) from TD-GC-MS and species quantified by LLE-GC-MS, see Appendix VIII for specific compounds from Fig. 15A. Both approaches for product characterization identified phenol, guaiacol, ethylguaiacol, acetovanillone, vanillic acid and two isomers of propylguaiacol. Guaiacol was found to be the most abundant with both methods. Of the compounds identified, eugenol and isoeugenol eluted during TD-GC-MS but were absent in the LLE-GC-MS, which could indicate that these compounds are not extracted into the DCM phase as seen in Fig. 16. It should also be noted that during analysis by LLE-GC-MS, homovanillic acid and two dimers were identified, that are not seen by TD-GC-MS which may be due to thermal decomposition.

A comparison of the final temperature fraction for each hydrothermally treated sample (Figs. 17-20) with the final fraction from the characterization of untreated lignin (Fig. 12) revealed a number of the same observed species with additional species observed with increasing temperature. Products that are seen in the lignin degradation products sample but were not detected in the raw lignin at the highest temperature fraction such as eugenol, propylguaiacol, ethylphenol and xylene are believed to be a direct result of the degradation of oligomeric products that did not evolve during the earlier steps.

To compare the results of TCA analysis (Fig. 12) to the TD-Py-GC-MS results, all the chromatograms (Figs. 17-20) were normalized to the response of IS. Although the results from the TD-Py-GC-MS analysis were not quantified, a semi-quantitative interpretation was performed based on the total peak areas of the chromatograms at varying temperatures with respect to an internal standard (IS). A notable difference was that products produced at higher hydrothermal treatment temperatures had a low amount of analytes evolving at 870 °C while on the TCA the 870 °C fraction had a significant wt. % for each sample. This difference could be due to low amounts of sample introduced to TD-Py-GC-MS and non-elutable products formed from lignin hydrotreatment, such as acids.

Although products from the 870 °C fraction were absent from Py-GC-MS for hydrotreated lignin at 275 °C and higher treatment temperatures. The trend was consistent with TCA showing that as the hydrothermal treatment temperature increased, a decrease in the fraction evolving at 870 °C was observed. A similar trend can be seen with an increase in the first temperature fraction (200 °C) as the hydrothermal treatment temperature increases.

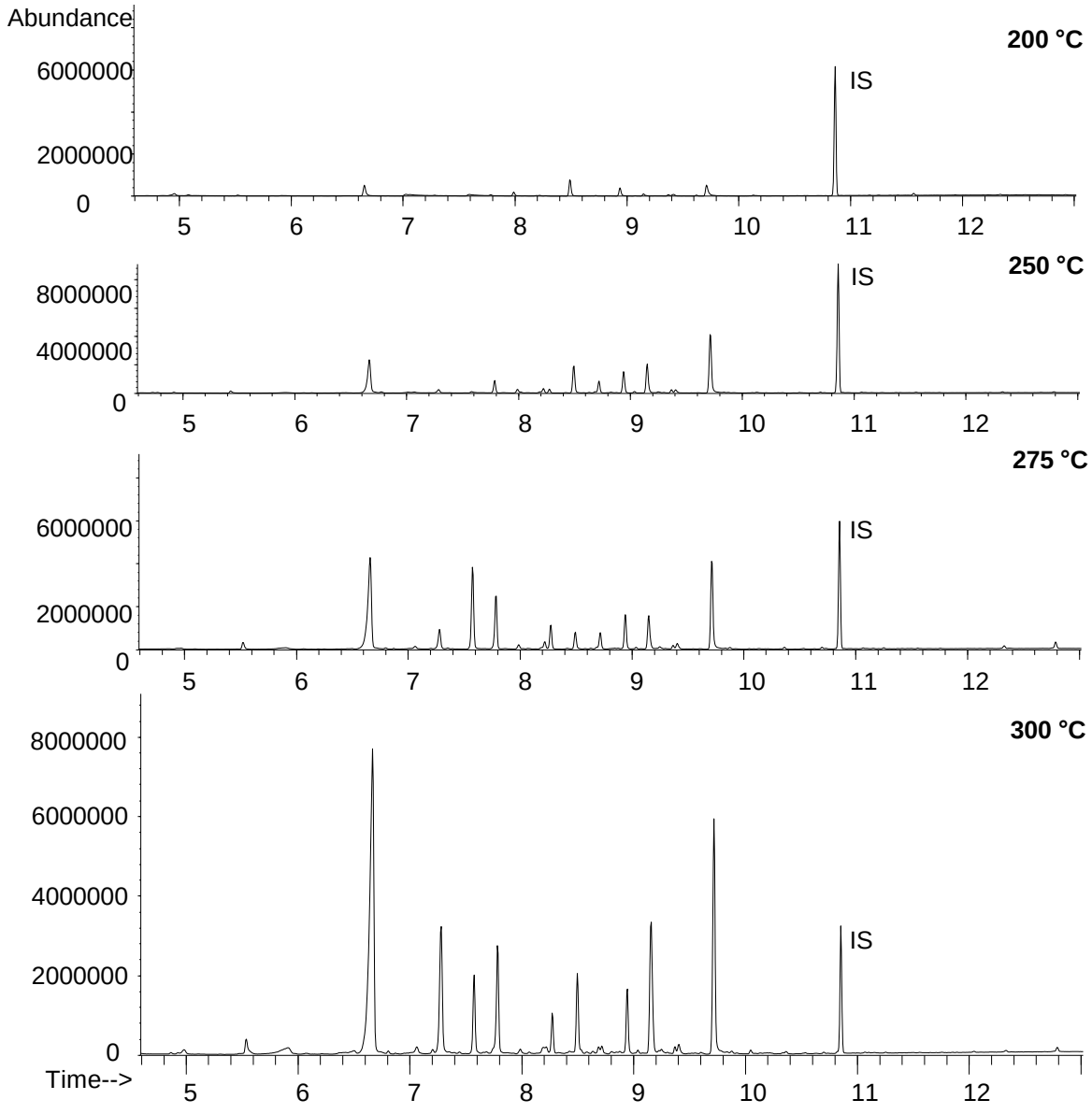


Figure 21. Comparison of the first temperature fraction (200 °C) from each the samples obtained at hydrotreatment temperature (200, 250, 275, and 300 °C)

With increase of hydrotreatment temperature, an increase in produced monomeric and dimeric products was expected. This trend was confirmed and it is demonstrated in Fig. 20 showing significant occurrence of these species in the volatile fraction evolving at 200 °C. Furthermore, by comparing the 200 °C fractions with that of untreated lignin (Fig.

12) any additional peaks not seen in untreated lignin may be viewed as a direct result of the hydrothermal treatment.

From hydrothermal treatment at 200 °C, three additional peaks were identified vs. untreated lignin; vinylguaiacol, homovanillyl alcohol, and 4-hydroxy-2-methoxycinnamaldehyde. Similarly, ethylguaiacol, eugenol, propylguaiacol and isoeugenol were identified additionally when treated at 200 – 250 °C. Ethylphenol also evolved in the samples treated at 250 – 275 °C and was not identified with untreated lignin.

We have also investigated the occurrence of polycyclic aromatic hydrocarbons (PAHs) as they are carcinogenic, result from incomplete combustion, and thus may be by-products in tars.[49] Interestingly, only a few PAHs were found in very low abundance in both untreated lignin and hydrothermally treated lignin only in the fraction obtained at 870 °C by Py-GC-MS (Fig. 20). The mass spectra for the PAHs found can be found in Appendix IX. The extracted MS ions characteristic of molecular weight of common PAHs with a mass to charge ratio (m/z) of 128, 142, 154, 178, and 202 were investigated. Ions above m/z = 202 (not shown) were not investigated as no PAHs were detected at m/z = 202. The PAHs identified based in mass spectra include naphthalene, methylnaphthalene, biphenyl, phenanthrene and anthracene.

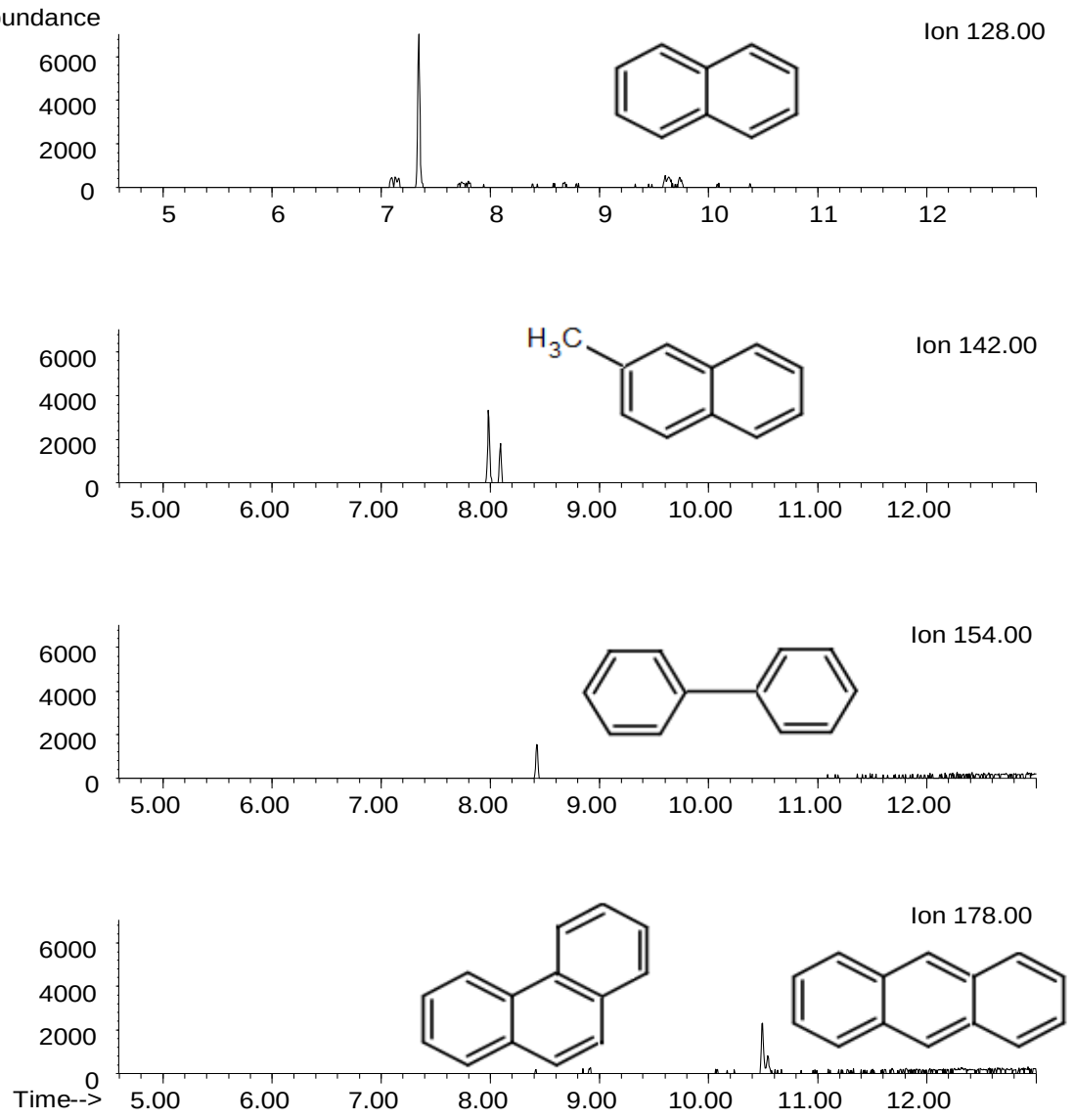


Figure 22. extracted ion chromatograms (m/z = 128, 142, 154, and 178) from lignin hydrotreated at 300 °C of the 870 °C fraction for the determination of polycyclic aromatic hydrocarbons (PAHs) formed obtained using Py-GC-MS

PAHs are commonly known for being produced as a result of incomplete combustion. Their identification in lignin pyrolysis products is not surprising as a significant portion (55 wt. %) of lignin does not evolve without the addition of oxygen (Fig. 9). Also, as mentioned previously, there are differences in the distribution of products in the thermal fractions of TD-Py-GC-MS, which could be caused by combustion with

naturally contained oxygen. The release of oxygen during this combustion at lower stages may promote the formation of PAHs at higher temperatures.

The formation of PAHs as a result of lignin pyrolysis has recently been reported where naphthalene, 1-methylnaphthalene, and anthracene were common products at pyrolysis temperatures above 800 °C.[49] PAH formation could also be a result of condensation reactions of lower MW aromatics such as phenol, toluene or xylene, which were seen in the same sample (Fig. 19).[49]

TD-Py-GC-MS is an approach to identify species that evolve with increasing temperature fractions that correspond to TCA. Both LLE-GC-MS and TD-GC-MS were able to identify nearly the same compounds with the exception of eugenol, homovanillic acid and two diaromatic compounds. This method also provides the ability to distinguish between the species originating from either untreated lignin or as a result of hydrothermal treatment. There was a direct correlation shown in Fig. 21 between the low MW aromatic compound production and increasing hydrothermal temperature. Lastly, it is probable that due to the absence of oxygen and abundance of benzenes, the PAH formation occurred during high pyrolysis temperatures.

CHAPTER V

CONCLUSIONS

In this work, we have developed a novel approach to the characterization of lignin and its degradation products by TCA. The method was optimized using lignin model compounds and applied to the analysis of untreated lignin. TGA allowed for method validation while showing the advantages of using TCA. Products of lignin degradation were analyzed by TCA and compared to LLE preparation for analysis by GC-MS as well as fractional TD-Py-GC-MS.

Analysis of lignin model compounds showed that solvent had little to no effect while it is preferable to load the samples on the quartz filter. Even simple monomers had fractions evolving at temperatures significantly higher than the boiling points and also only in the presence of oxygen (pyrolyzed/coked fractions) which did not appear to be affected by a change of the initial temperature step.

TCA showed a large fraction of lignin that evolved only in the presence of oxygen (55 wt. %), which is neglected by other approaches to the characterization of lignin. Analyzing lignin on TGA with a similar heat ramp showed that a similar thermal profile could be obtained. However, TCA has an advantage as it is selective for carbon and ignores the effect of impurities and naturally occurring oxygen.

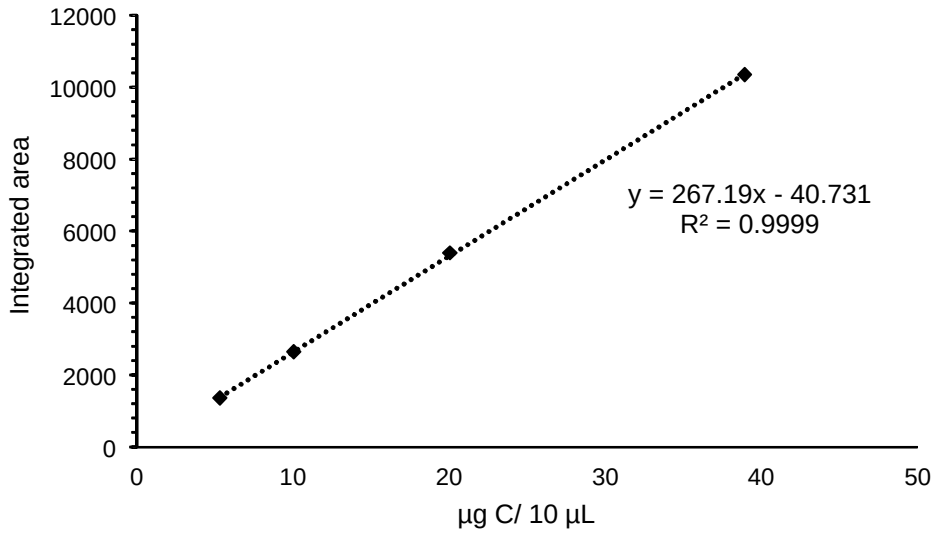
The analysis of hydrothermally treated samples on TCA provided a comprehensive characterization of lignin degradation products. TCA allowed for product characterization through different temperature fractions showing monomer formation with increasing

temperature as well as repolymerization effects. Although it was not a perfect match, there was a strong correlation between the total wt. % recovered by LLE-GC-MS and TCA, thus allowing detailed identification of products evolving in the early fractions (200 and 300 °C) of TCA. TD-Py-GC-MS allowed for determination of compounds that were a direct result of hydrothermal treatment and not caused by any unreacted lignin remaining in the sample. Lignin hydrothermally treated at 300 °C evolved significantly more species at lower temperatures during TD-Py-GC-MS than that of hydrothermal treated samples at 200 °C, which indicated the formation of monomers at higher temperatures.

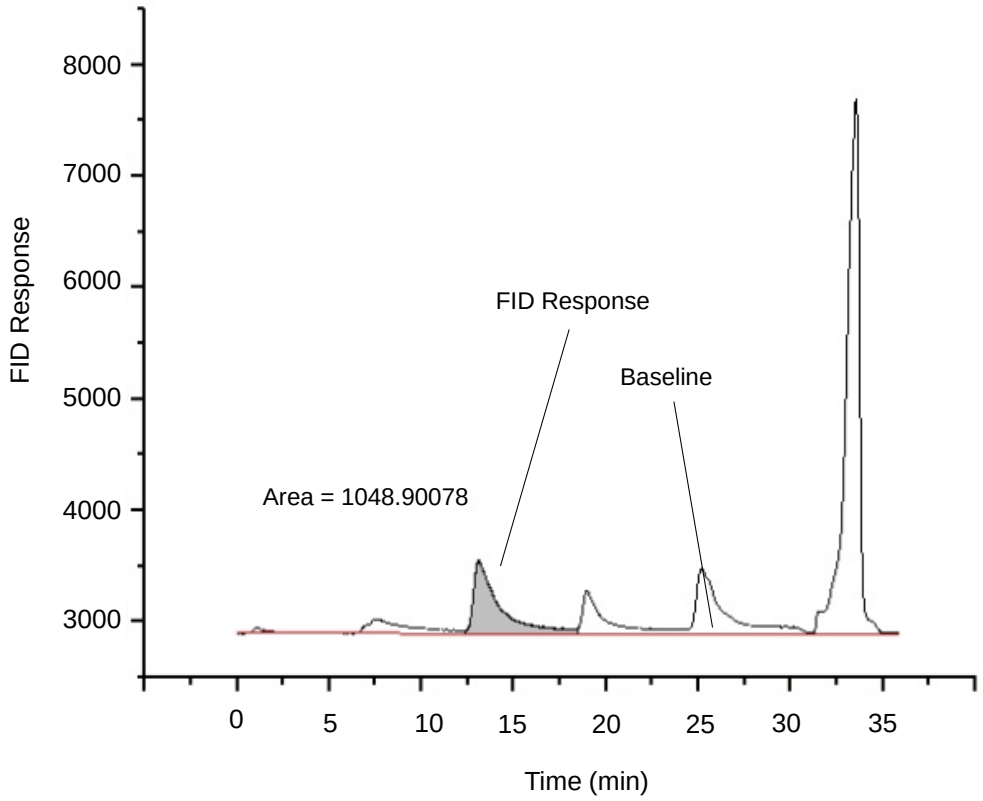
Overall, TCA is a novel approach which is simple and comprehensive characterization of lignin and its degradation products. It provides a thermal profile, which can semi-identify products formed based on temperature evolved while providing quantification with a mass balance closure. When used in combination with other methods such as LLE-GC-MS or TD-Py-GC-MS, species can be further identified thus providing an inclusive characterization of lignin and its degradation products.

APPENDICES

Appendix I. Calibration curve used for the integration of peak areas based on the integration from OriginLab® Origin Pro 9.1



Appendix II. Example of integration calculation using OriginLab® Origin Pro 9.1 for the 400 °C fraction from the analysis of lignin.



After a base line has been created, the peak area can be integrated to the baseline which is then used with the sucrose calibration (Appendix I) to determination of carbon evolved in fraction.

$$1048.9 = 267.19\ x - 40.731$$

$$x = 4.0781\ \mu g\ C$$

Procedure for using origin pro is as follows:

Creating a baseline for the curve

Go to Analysis>Peaks and Baseline>Peak Analyzer>Open Dialog. This brings up the Peak Analyzer window. On the top pane of the window the wizard is shown highlighting the steps you will take in the process of creating the baseline for your curve. In the first step you will select the goal of this process:

Recalculate "Manual"

Goal "Create Baseline"

Input Your graph/curve (Example: [Graph1]1!1"Heat Flux")

Push next to move onto the next step of the Peak Analyzer wizard: Baseline Mode. In this pane select the following:

Baseline Mode "User Defined"

Snap to Spectrum Uncheck

Baseline Anchor Points

Method "2nd Derivative"

Smoothing Window Size 1 Keep "Auto" checked

Threshold 0.05 Keep "Auto" checked

Current # of points 0

Enable Auto Find Check (only for initial peak find)

Number of pts to find 8

Now push the “Find” button. You will see the baseline anchor points appear along your curve. If you are satisfied with the placement of these points you may go on to integrating the peak areas of the curve. If not, then you may do the following:

1) Uncheck the “Enable Auto Find” option. This will enable the “Add”, “Modify/Del” and “Clear All” buttons below

2) To add a baseline anchor point push the “Add” button. This brings you to your graph window and a crosshair cursor will be shown. To add an anchor point move the cursor to the desired location and double-left click.

3) To move an already existing anchor point select “Modify/Del”, bringing you back to your graph window. Select the point you wish to move by clicking and holding down the left mouse button. Move the point to the desired location and release the left mouse button to set the new location.

4) You can view the anchor point info at anytime by selecting the “Anchor Points Info..” button.

Integrating Peak Areas (Using a User Defined Baseline)

This procedure is for integrating peak areas of a curve based on a user defined baseline that is already added to the curve (see section above for instruction on creating the user defined baseline).

Go to Gadgets>Integrate.., this brings up the Data Exploration: addtool_curve_integ window. In the Integration Tab set the following:

Fit Limits To “Data Points”

Area Type “Mathematical Area” (algebraic sum of trapezoids) or

“Absolute Area” (sum of absolute trapezoid values)

Show

Show Integrated Area Leave checked

Integral Curve None

In the Baseline tab select the following:

Mode “Use Existing Dataset”

DatasetSelect the baseline you created (Example: [Graph2]1!2”Baseline of Heat Flux”)

Range “Curve within ROI”

Appendix III. Calculation for determination of volume in a vessel (Fig. 4C) for the analytical static batch reactor.

Determination of cap volume through mass substitution.

1. Mass of H_2O to fill the cylinder and one cap = 3.5713 g

2. Density of H_2O at 20.4 °C = 0.9981 g/mL

3. Volume of H_2O in cylinder w/ cap = 3.578 mL

4. Cylinder volume = π x 6.325 cm x $\left(\frac{0.71\ \text{cm}}{2}\right)^2$ = 2.5 cm^3 (mL)

5. Volume of cap = (3) – (4) = 1.1 mL

6. Vessel volume = (4) + 2 x (5) = 4.7 mL

Appendix IV. Calculation for determination of pressure and % water phase inside vessel at given temperature.

Saturation conditions from NIST

Temperature °C	200	250	275	300
Pressure (Bar)	15.55	39.76	59.46	85.88
Density (liquid) (g/mL)	0.8647	0.7989	0.759	0.7121
Density (Vapor) (g/mL)	0.00786	0.01997	0.03052	0.04617

Determination of pressure and water phase inside vessel for an experiment at 300 °C

1. Density of lignin was calculated by mass of lignin to fill known volume (graduated cylinder and found to be 0.5 g/mL
2. Volume occupied by lignin = 0.25g x $\frac{1\ \text{mL}}{0.5\ \text{g}}$ = 0.5 mL
3. Assuming lignin is non-compressible and H_2O will expand to fill the remainder of vessel upon heating the density of H_2O within the vessel during heating:

$$\text{Density of } H_2O = \frac{\text{Mass of water}}{V_{\text{vessel}} - V_{\text{lignin}}} = \frac{2.8\ \text{g}}{4.7\ \text{mL} - 0.5\ \text{mL}} = 0.667\ \text{g/mL}$$

Since 0.667 g/mL < 0.7121 g/mL it is known the vessel pressure is < 85.88 bar

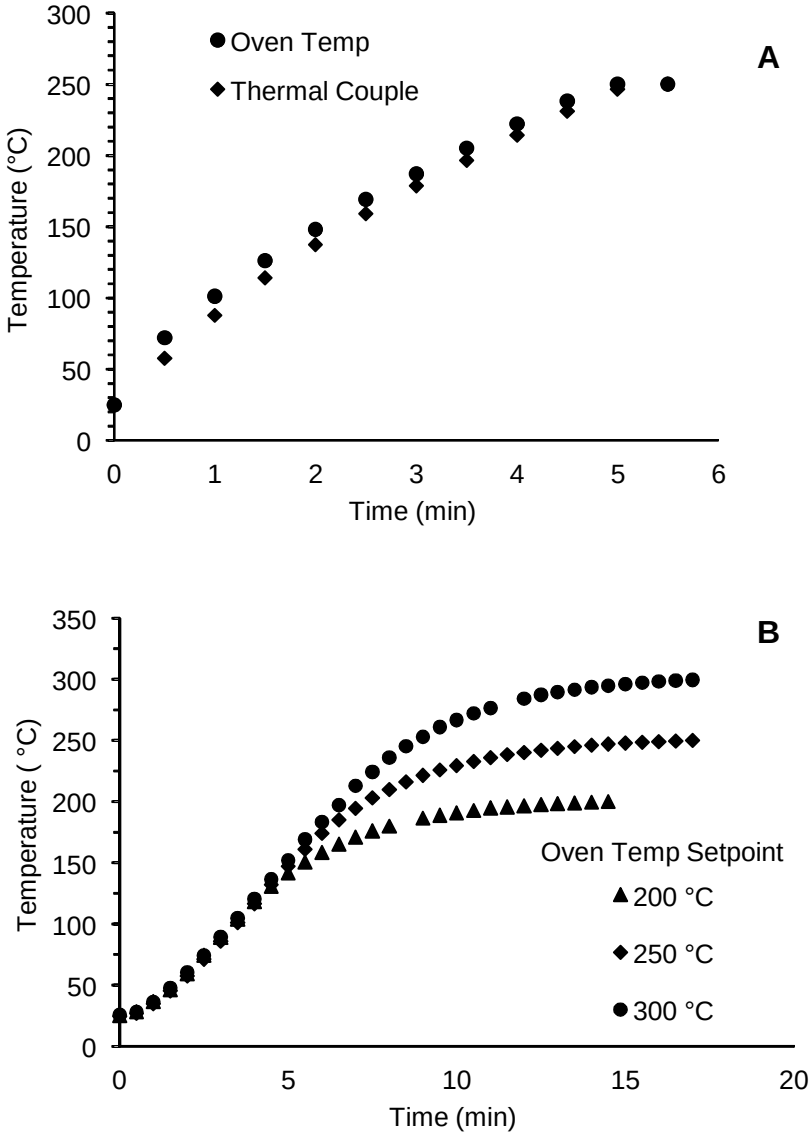
4. The percent of liquid phase the water is can be calculated with the following equation:

$$\%\ H_2O \text{ liquid phase} = \frac{D_{\text{sample}} - D_{\text{vapor}}}{D_{\text{liquid}} - D_{\text{vapor}}} \times 100 = \frac{0.667\ \frac{\text{g}}{\text{mL}} - 0.0462\ \frac{\text{g}}{\text{mL}}}{0.7121\ \frac{\text{g}}{\text{mL}} - 0.0462\ \frac{\text{g}}{\text{mL}}} \times 100 = 93.2\%$$

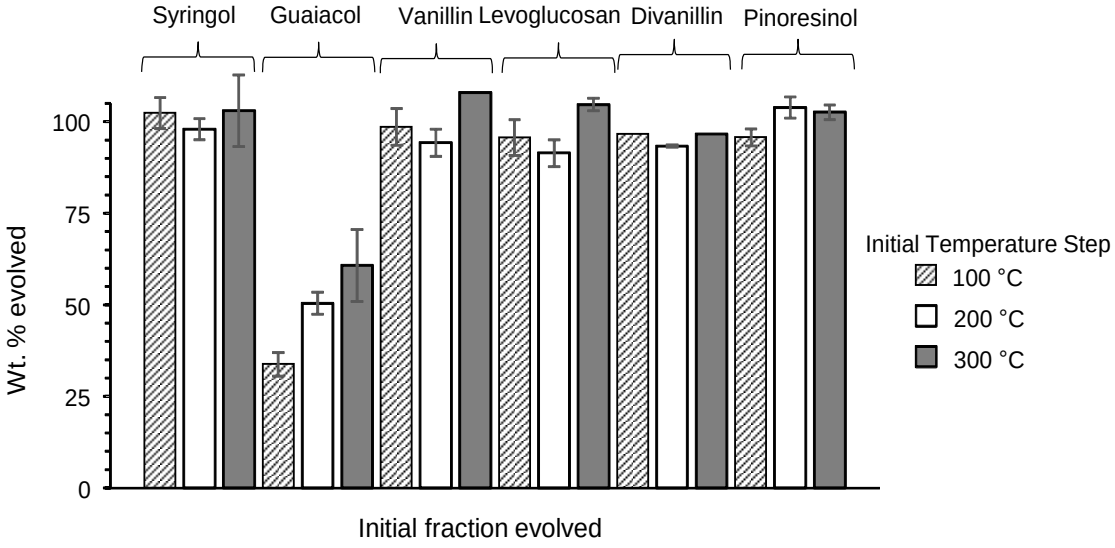
Operating conditions

Oven Temperature (°C)	Mass Lignin (g)	Water Volume (mL)	Vessel Pressure (Bar)	Percent Liquid Phase
200	0.10	3.2	< 16	82
250	0.25	2.9	< 40	86
275	0.25	2.8	< 60	90
300	0.25	2.8	< 86	97

Appendix V. A) Comparison of oven temperature based on internal thermal couple vs oven temperature measured by vessel temperature probe. B) Actual vessel temperature vs set oven temperature. The oven can reach 250 °C in ~ 5 minutes while the internal vessel temperature takes ~15 minutes.



Appendix VI. Wt. % of fractions evolving during the first fraction. Below are results from the first, 700 and 550 – 850 °C fractions.



		TCA Temperature Fractions wt. %		
Compound	**Initial Step**	**Initial Step**	**700 °C**	**550-850 °C w/ O_2**
Syringol	100	90 ± 2	7 ± 1	3 ± 0.6
	200	94 ± 1	4 ± 0.8	2 ± 0.4
	300	90 ± 6	8 ± 7	2 ± 0.4
Guaiacol	100	83 ± 4	13 ± 3	4 ± 1.1
	200	96 ± 1	3 ± 1	1 ± 0.1
	300	95 ± 1	4 ± 1	1 ± 0.4
Vanillin	100	95 ± 2	4 ± 1	1 ± 0.5
	200	96 ± 1	3 ± 1	1 ± 0.4
	300	99 ± 0.1		1 ± 0.1
Levoglucosan	100	88 ± 0.5	10 ± 0.6	2 ± 0.3
	200	90 ± 1	8 ± 0.3	2 ± 0.3
	300	87 ± 1	11 ± 1	2 ± 0.3
Pineoresinol	100	0.3 ± 0.1	79 ± 1	20 ± 1
	200	1 ± 0.1	80 ± 1	19 ± 1
	300		82 ± 0.4	18 ± 0.4
Divanillin	100	4.6 ± 0.7	79 ± 1	16 ± 0.3
	200	2 ± 1	83 ± 1	15 ± 0.4
	300	5 ± 0.6	79 ± 1.5	16 ± 1.0

Appendix VII. Determination of moisture in lignin from weight difference and TGA analysis.

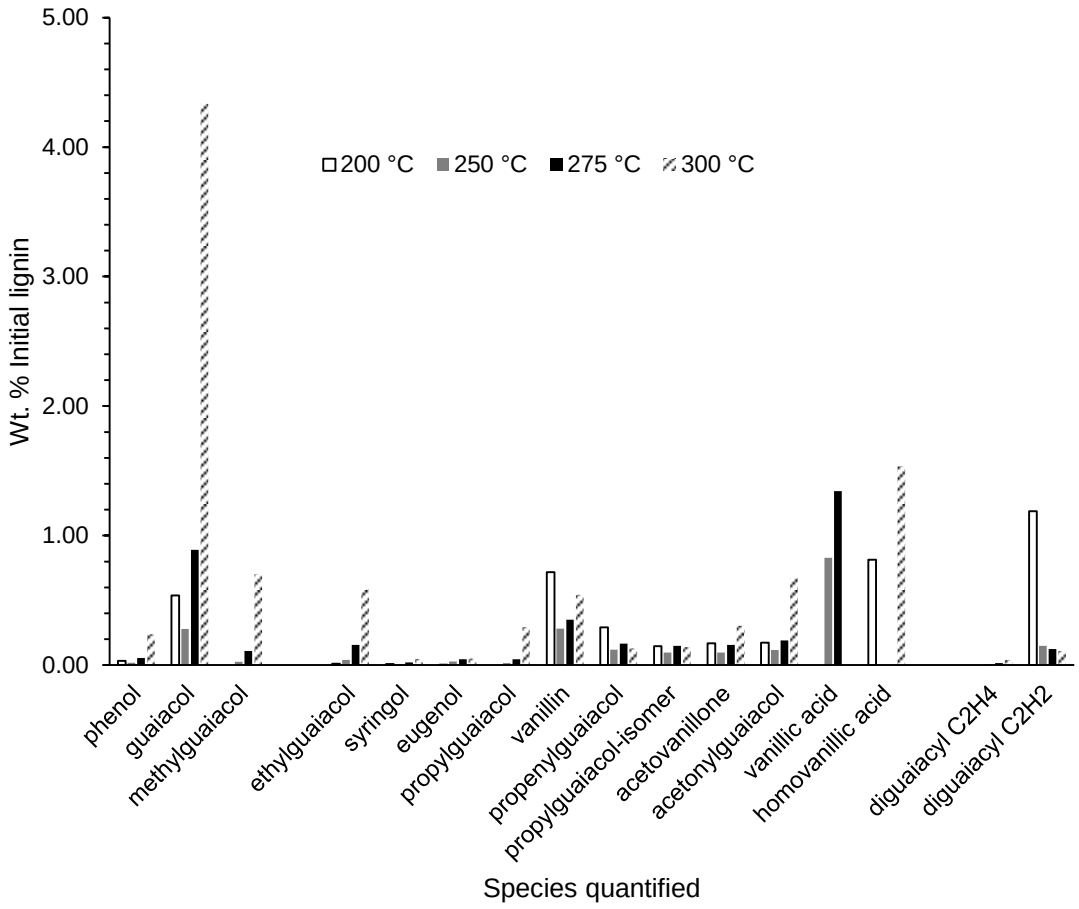
Measurements taken from OHMAUS MB25 Moisture analyzer

	Lignin mass (g)	Mass lignin after drying	% Mass Loss
	0.510	0.491	3.820
	0.505	0.485	3.960
	0.525	0.505	3.810
Average	0.5133	0.4935	3.863
St. Dev	0.010	0.010	0.084
RSD	2	2	2

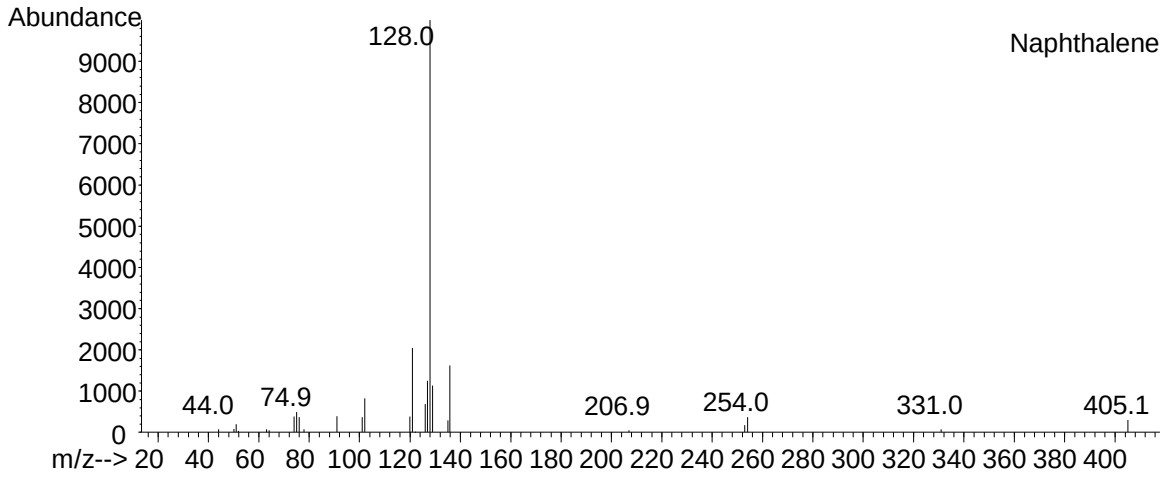
Data from TGA analysis

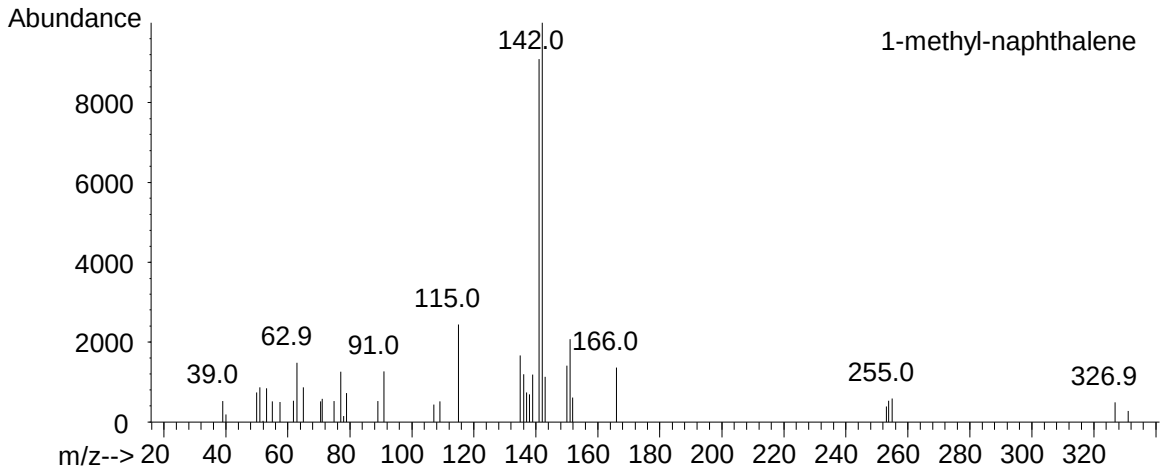
	Initial Mass (g)	Mass at after initial weight loss (g)	% Mass loss
	18.80276	18.14188	3.515
	17.57822	16.96686	3.478
	33.48068	32.28805	3.562
Average	23.2872	22.4656	3.518
St. Dev	8.849	8.527	0.042
RSD	38	38	1

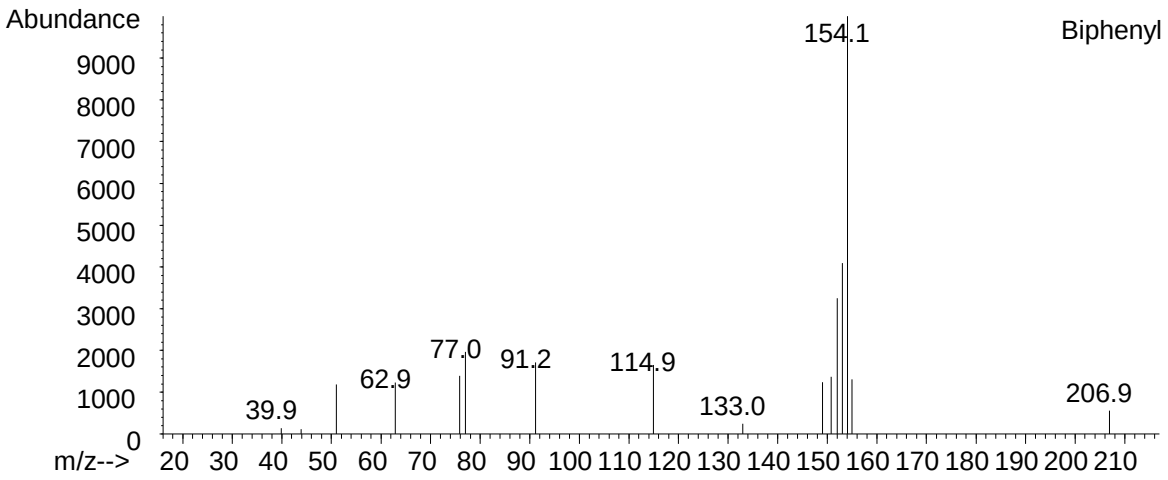
Appendix VIII. Quantification of products from varying hydrothermal treatment experiments of lignin by LLE-GC-MS using calibration with standards.

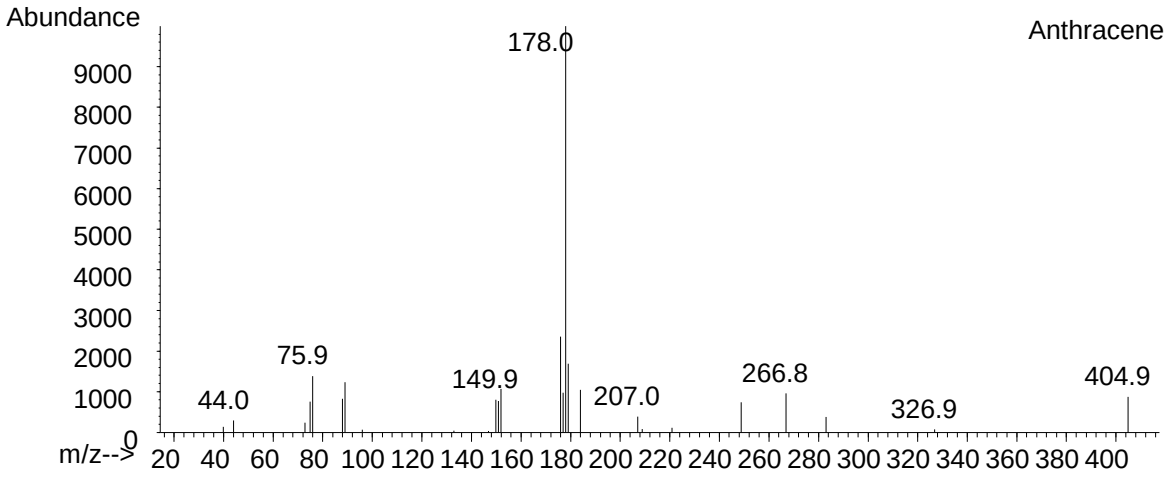


Appendix IX. Mass spectras of PAHs identified during pyrolysis at 870 °C by Py-GC-MS.






Abundance
Biphenyl
154.1
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
77.0
91.2
114.9
62.9
39.9
133.0
206.9
m/z-->
20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210


Abundance
Anthracene
178.0
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
75.9
149.9
266.8
404.9
44.0
207.0
326.9
m/z-->
20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400

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