Effect of torrefaction temperature on lignin macromolecule and product distribution from HZSM-5 catalytic pyrolysis

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Torrefaction is a low-temperature process considered as an effective pretreatment technique to improve the grindability of biomass as well as enhance the production of aromatic hydrocarbons from Catalytic Fast Pyrolysis (CFP). This study was performed to understand the effect of torrefaction temperature on structural changes in the lignin macromolecule and its subsequent influence on in-situ CFP process. Lignin extracted from southern pine and switchgrass (via organosolv treatment) was torrefied at four different temperatures (150, 175, 200 and 225 ⁎C) in a tubular reactor. Between the two biomass types studied, lignin from pine appeared to have greater thermal stability during torrefaction when compared with switchgrass lignin. The structural changes in lignin as a result of torrefaction were followed by using FTIR spectroscopy, solid state CP/MAS ^{13}C NMR, ^{31}P NMR spectroscopy and it was found that higher torrefaction temperature (200 and 225 ⁎C) caused polycondensation and de-methoxylation of the aromatic units of lignin. Gel permeation chromatography analysis revealed that polycondensation during torrefaction resulted in an increase in the molecular weight and polydispersity of lignin. The torrefied lignin was subsequently used in CFP experiments using H^+ZSM-5 catalyst in a micro-reactor (Py-GC/MS) to understand the effect of torrefaction on the product distribution from pyrolysis. It was observed that although the selectivity of benzene-toluene-xylene compounds from CFP of pine improved from 58.3% (torrefaction temp at 150 ⁎C) to 69.0% (torrefaction temp at 225 ⁎C), the severity of torrefaction resulted in a loss of overall aromatic hydrocarbon yield from 11.6% to 4.9% under same conditions. Torrefaction at higher temperatures also increased the yield of carbonaceous residues from 63.9% to 72.8%. Overall, torrefying lignin caused structural transformations in both type of lignins (switchgrass and pine), which is ultimately detrimental to achieving a higher aromatic hydrocarbon yield from CFP.

1. Introduction

Biomass has been considered to be a sustainable carbon source for producing chemicals and liquid intermediates through fast pyrolysis, which could be upgraded to renewable fuels and other valuable products [1–7] . It consists of three major components cellulose, hemicellulose and lignin, whose composition varies from one species to another. Cellulose is a linear polymer composed of 1,4 beta-D linked anhydroglucose subunits, whereas hemicellulose is a branched, amorphous polysaccharide made of five carbon sugar compounds. Lignin is the third constituent, which can be defined as an amorphous aromatic polymer of phenyl propane units. It is a complex and high molecular weight polymer formed by the dehydrogenation of hydroxyl cinnamyl alcohols such as coniferyl and sinapyl alcohols. The degree of methoxylation differs between the various lignin precursors and various types of intermolecular linkages (β-O-4, α-O-4, 5-5, β-5, and β-β) can occur, which varies in composition between different types of biomass. The decomposition of lignin results in the formation of compounds such as guaiacol, vanillin, syringol, anisole and other phenolic compounds. Due to such complexity in the structure of biomass, the thermal breakdown of these constituents (cellulose, hemicellulose and lignin) during pyrolysis results in the formation of a complex mix-

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ture of condensable compounds along with non-condensable gases and char.

This liquid intermediate from pyrolysis (bio-oil) suffers from certain undesirable properties such as [1] high oxygen content (30-40%) making the product immiscible with conventional fuels; [2] presence of organic acids, causing corrosion and instability during storage; [3] low heating value (19 MJ/kg) when compared to fossil-based fuels; [4] alkali and alkaline earth metals (Na, K, Ca and Mg) in biomass, which alters pyrolysis chemistry. A number of studies in the past decade have focused on improving these properties by deoxygenating the bio-oil from pyrolysis through catalytic upgrading and hydrodeoxygenation [7–13] . Promising catalysts including zeolites are being actively studied for in-situ catalytic fast pyrolysis (CFP) to upgrade the pyrolysis vapors and produce a highly deoxygenated liquid product. However recently, mild thermal pretreatment (torrefaction) has been suggested as an effective process to improve the properties of biomass before it is used as a feedstock for pyrolysis. Some of the advantages of torrefaction, such as [1] improved grindability of biomass; [2] lower O/C ratio; [3] improved biomass hydrophobicity; make it a promising technique to improve the economics of biomass-to-energy conversion.

During torrefaction, biomass is generally heated at moderate temperatures (200–300 C) in an inert environment, which results in reduced oxygen content in the torrefied biomass mainly due to extensive decomposition of hemicellulose in this temperature range. Hemicellulose decomposition products such as acetic acid, furfural, water, CO and CO_2 are released from biomass during this process [14] . Meanwhile, the structure of cellulose remains relatively intact during this process since higher temperatures (>300 C) are required for complete decomposition. Recent studies on torrefaction of biomass have shown that torrefaction is an effective pre-treatment which improves the yield and selectivity of aromatic hydrocarbons from CFP of torrefied biomass [15–20] . Recent publications by Neupane et al. [15] and Srinivasan et al. [19] discussed the effect of torrefaction parameters such as residence time and temperature on the structural changes in biomass and its subsequent influence on the product distribution from catalytic pyrolysis of biomass. Neupane et al. observed higher carbon yield of aromatic hydrocarbons from CFP of torrefied biomass and proposed that this could be a result of de-etherification and demethoxylation of lignin during torrefaction. However, since very limited studies have focused on the torrefaction and CFP of individual components of biomass, this hypothesis could not be confirmed. Further, the structural changes in lignin as a function of torrefaction at various temperatures is also not clear. Thus, the objective of this study was to understand the effect of torrefaction temperature on the structural changes in lignin and its influence on the product distribution from pyrolysis. Torrefaction of lignin extracted from southern pine and switchgrass through organosolv treatment was performed in a tubular reactor. Subsequently, the non-catalytic and in-situ CFP of torrefied lignin were performed in a micro-pyrolyzer.

2. Materials and methods

2.1. Biomass preparation

The southern pine used in this study was obtained from a local wood chipping plant in Opelika, Alabama and switchgrass was obtained from E.V. Smith Research Center, Macon County, Alabama. Biomass was first air dried for 72 h and a hammer mill (New Holland Grinder Model 358) fitted with a 1.58 mm (1/16 in.) sized screen was used to grind the samples. Subsequently, it was fractionated using a sieve shaker and particles in the desired size range (400 μm–840 μm) were used for organosolv lignin extraction.

2.2. Organosolv extraction

A known amount (350 g) of the biomass (dry weight) was soaked for 24 h in 65% ethanol and 1.0% (w/w) sulfuric acid (based on biomass) in a solid to liquid ratio of 1:7. The mixture containing biomass and liquor was loaded in a 4.0 L Parr reactor and pretreated at 170 C for 1 h with a stirring rate of 60 rpm. After pretreatment, the reactor was cooled in a water bath and the resulting slurry was separated into a solid fraction and a liquid fraction by filtration. The solid fraction was washed with warm ethanol three times to remove the extractable lignin and stored at – 20 C. To prepare ethanol organosolv lignin (EOL) from biomass, 3-fold volume of water was added to organosolv spent liquor (the liquid fraction) after pretreatment. Organosolv lignin was precipitated and collected by vacuum filtration on Whatman No. 1 filter paper, washed with warm water to remove the water-soluble compounds and then dried. Since the pyrolysis was to be performed in a micro-pyrolyzer, the lignin had to be sieved further using a 200 mesh (74 μm) and the fraction that passed was used for characterization, torrefaction and pyrolysis experiments in this study.

2.3. Lignin torrefaction and characterization

Lignin from pine and switchgrass was torrefied at four temperatures (150, 175, 200, 225 C) for 15 min in a tubular reactor (18 in. long, 1 in. outer diameter) placed in a programmed furnace (Thermo Scientific model TF55035A-1). 5 g of organosolv lignin was used for torrefaction at each condition, and the volatiles released from lignin during torrefaction were swept away by nitrogen gas flow at 1 L/min. Treatment time began when the furnace reached the desired set point. At the end of the treatment time, the torrefied samples were pulled from the furnace and immediately placed in desiccators to prevent further treatment and combustion. The samples (shown in Supplementary information Fig. S1) were weighed before and after torrefaction to calculate the mass loss as a result of torrefaction using a microbalance (Mettler Toledo, model XP6). Moisture and ash contents were determined for the lignin samples according to ASTM E872 and E1755 standards, respectively. Ultimate analysis to measure the carbon, hydrogen, nitrogen, oxygen and sulfur contents was performed for raw and torrefied lignin using a CHNS elemental analyzer (Thermo Scientific, model Flash 2000). Component analysis to measure extractives, cellulose, hemicellulose and lignin contents was performed according to Laboratory Analytical Procedure (LAP) developed by National Renewable Energy Laboratory [21] . Thermogravimetric (TG) analysis to calculate the weight loss as a function of temperature of raw and torrefied lignin was performed (TA Instruments, 2050 TGA) with a heating rate of 10 C/min and helium flow rate of 20 mL/min. FTIR analysis to study the structure of raw and torrefied lignin was done using a Perkin Elmer Spectrum model 400 (Perkin Elmer Co., Waltham, MA). Each spectrum was recorded after 32 scans from 4000 to 650 cm^{-1}, by applying a vertical load on the sample at room temperature. Solid-state CP/MAS ^{13}C NMR analysis was performed on a Bruker Avance III 400 MHz spectrometer, according to the methods previously described by Neupane et al. [15] .

The lignin samples for Gel Permeation Chromatography (GPC) analysis were manually milled in a jar for 5–10 min. The molecular weight of lignin was analyzed by GPC after lignin acetylation. The derivatization of lignin was conducted on a basis of 10 mg lignin in 1 mL of 1:1 pyridine/acetic anhydride in the dark at room temperature for 24 h, 200 RPM. The solvent/reagents were removed by co-evaporation at 45 C with ethanol, several times, using a rotatory evaporator until dry. The resulting acetylated lignin was dissolved in tetrahydrofuran (THF) and the solution was filtered through 0.45 μm membrane filter before GPC analysis. The hydroxyl groups in lignins were quantitated by ^{31}P

NMR after lignin phosphitylation. In detail, the lignin samples were vacuum dried at 45 C overnight before phosphitylation and 25.0 mg of lignin was accurately weighted into a 4-mL viale 0.5 mL of a prepared stock solution of pyridine/deuterated chloroform (1.6/1.0, v/v) including 1 mg/mL Cr(acac) $_3$ and 4 mg/mL internal standard (endo N-hydroxy-5-norbene-2,3-dicarboxylic acid imide) was added to dissolve lignin. The phosphitylation was performed by adding 50 μL of the phosphitylating reagent TMDP (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane). Quantitative ^{31}P NMR spectra were acquired on a Bruker Advance 400 MHz spectrometer equipped with a BBO probe with 64-scans and a total runtime of 28 min. All chemical shifts reported are relative to the product of TMDP with water, which has been observed to give a sharp signal in pyridine/CDCl $_3$ at 132.2 ppm.

2.4. Catalyst

A commercially available HZSM-5 catalyst (CBV 2314 with a SiO_2/Al_2O_3 ratio of 23:1, Zeolyst, USA) was used in the in-situ CFP experiments. The catalyst was sieved using a 200 mesh and the fraction that passed through the sieve (<74 μm) was used in this study. It was then calcined for 5 h at 550 C in a muffle furnace to convert the catalyst to the acid form prior to use. The lignin/catalyst mixture for in-situ CFP experiments was prepared by mixing 50 mg of the lignin and 200 mg of the catalyst using an ultrasonic bath (VWR Scientific, catalog no. 97043-960) to get a mixture having a lignin to catalyst ratio of 1:4. A microbalance with sensitivity of 0.001 mg (Mettler Toledo, XP6) was used to measure the sample weight.

2.5. Experimental procedure

Pyrolysis experiments were carried out on a Tandem micro-reactor system (Frontier Laboratories, Rx-3050 TR), which was connected to a gas chromatograph (Agilent Technologies, 7890A). Fig. 1 shows a schematic diagram of the system used in this study containing two quartz pyrolysis tube reactors (4.7 mm ID, 114 mm length) arranged in series.

The reactors were equipped with independent temperature control between 40 and 900 C and an independent temperature controlled interface between the two reactors to prevent condensation of pyrolysis products. Samples were placed in deactivated stainless steel sample cups and loaded into the reactor. Helium gas flow for 45 s purged the reaction environment and the sample cup was then dropped into the pyrolysis reactor (drop time of 15–20 milliseconds [22]). The products of pyrolysis from the first reactor were swept into a GC–MS using helium gas flow for analyzing the product composition. In the non-catalytic experiments, 0.5 mg of the lignin was pyrolyzed in the first reactor, and the second reactor was empty. For in-situ CFP experiments in this study, approximately 2.5 mg of the lignin/catalyst mixture (lignin:catalyst – 1:4) was pyrolyzed in the first reactor and the second reactor was empty. The second reactor was also maintained at the same temperature as the interface at 350 C in order to prevent condensation of pyrolysis vapor. A gas chromatograph (Agilent Technologies, 7890A) equipped with an Agilent DB 1701 capillary column (60 m × 0.250 mm and 0.250 μm film thickness) was used to separate and analyze condensable compounds from pyrolysis. A split ratio of 1:100 was used for sample injection into the column and the GC inlet was maintained at 250 C. The GC oven was programmed to start at 40 C and hold for 3 min, after which it was ramped at 5 C/min up to the final temperature of 270 C. The final temperature was held for 6 min and the overall time of the oven program was 55 min. The column was connected to a mass spectrometer (Agilent Technologies, 5975C) for compound identification and quantification by using calibration standards. Some of the major products identified (non-catalytic pyrolysis products from lignin/aromatic hydrocarbons from in-situ CFP) were quantified using pure compounds purchased from Sigma-Aldrich (St. Louis, Missouri). Calibration factors for quantification were prepared by using three different concentrations of the standards. A Porous Layer Open Tubular (PLOT) column (Agilent Technologies, GS-GasPro) was used to analyze the composition of non-condensable gas (NCG) products (CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8 and C_4H_8) and a standard gas mixture of these NCG was used to calibrate the yield of non-condensable gases. The weight of the sample cup before and after the experiment was measured in order to calculate the char yield. However, it was not possible to distinguish between pyrolysis char and catalytic coke in the in-situ CFP experiments which were performed with the catalyst mixed along with the lignin in the sample cup.

Each experiment was performed in duplicate in order to obtain a standard deviation for the results and verify the reproducibil-

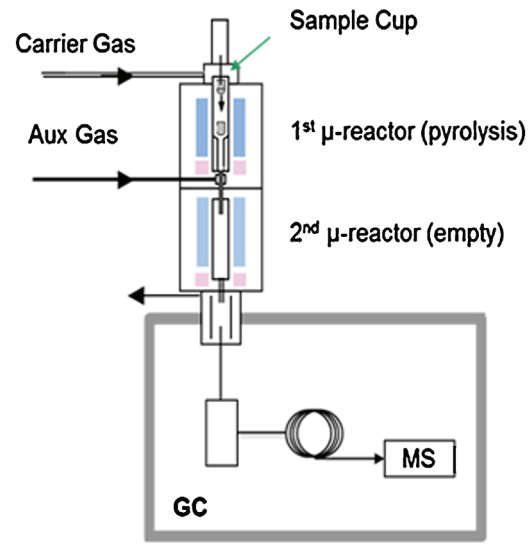

Fig. 1. Schematic of tandem micro-reactor used in this study.

Table 1
Nomenclature used for samples torrefied at different temperatures.

Nomenclature	Torrefaction Temperature (C)	Description
RLP	Control	Raw (Non-torrefied) Lignin Pine
TP 150	150	Torrefied Lignin Pine – 150 C
TP 175	175	Torrefied Lignin Pine – 175 C
TP 200	200	Torrefied Lignin Pine – 200 C
TP 225	225	Torrefied Lignin Pine – 225 C
RLS	Control	Raw (Non-torrefied) Lignin Switchgrass
TS 150	150	Torrefied Lignin Switchgrass – 150 C
TS 175	175	Torrefied Lignin Switchgrass – 175 C
TS 200	200	Torrefied Lignin Switchgrass – 200 C
TS 225	225	Torrefied Lignin Switchgrass – 225 C

Table 2
Ultimate analysis of raw and torrefied samples. [a]

Feedstock	Carbon (wt.%)	Hydrogen (wt.%)	Oxygen (wt.%)
RLP	65.52 [A]	5.63 [A]	28.60 [A]
TP 150	65.90 [A]	5.44 [B]	28.42 [A]
TP 175	66.29 [B]	5.41 [B]	28.07 [B]
TP 200	67.34 [C]	5.41 [B]	27.03 [C]
TP 225	67.78 [C]	5.33 [C]	26.68 [C]
RLS	64.88 [A]	5.69 [A]	28.79 [A]
TS 150	65.17 [B]	5.62 [B]	28.58 [A]
TS 175	65.77 [C]	5.68 [A]	27.95 [B]
TS 200	65.83 [C]	5.63 [B]	27.92 [B]
TS 225	66.59 [D]	5.57 [A]	27.23 [C]

Nitrogen values included in Supplementary information Table S1.
[a] Results in dry, ash-free basis. Values connected by same letter are not statistically different.

Table 3
Mass yield of torrefied samples. [a]

Feedstock	Mass yield (wt.%)
TP 150	97.90
TP 175	94.34
TP 200	92.41
TP 225	89.33
TS 150	95.19
TS 175	92.78
TS 200	89.11
TS 225	87.16

[a] Dry, ash-free basis. Single run only.

ity of the data. Three factors of interest at various levels – 1) type of biomass used (pine, switchgrass); 2) torrefaction temperature (150, 175, 200, 225 C); and 3) with and without catalyst – were the focus of this study. The nomenclature of the samples in this study is shown in Table 1. Results labelled as CFP are from experiments using HZSM-5 as the in-situ catalyst. JMP software (SAS Institute, Cary, North Carolina) was used to perform statistical analysis of the results such as ANOVA, Tukey's HSD at a 95% confidence interval. However due to the accuracy of the results from using the micro-pyrolyzer, the standard deviation of the results was less than 5% and is not shown. The ratio of carbon in a specific product or group to the carbon contained in the feedstock is the total carbon yield of that product or group and is used to report the results from CFP experiments. Selectivity of a particular aromatic hydrocarbon is defined as the ratio of moles of carbon in that product to the total moles of carbon in all aromatic hydrocarbons produced. The overall carbon balance for most of the experiments was close to or above 90% with the remaining fraction including large molecular weight compounds not identified by the GC.

3. Results and discussion

3.1. Lignin characterization and mass yield after torrefaction

Raw lignin obtained from organosolv treatment of pine was measured to have moisture and ash contents of 2.6 ± 0.15 (wt.% on wet basis) and 0.65 ± 0.09 (wt.% on dry basis), while lignin from switchgrass had moisture and ash contents of 1.8 ± 0.22 (wt.%) and 1.2 ± 0.18 (wt.%), respectively. Torrefaction produced a small increase in the carbon content of lignin along with a corresponding decrease in the oxygen content as shown in Table 2, possibly due to the removal of moisture and volatile oxygenates during torrefaction. Although lignin generally does not decompose completely below 300 C, mass yield results from Table 3 shows that at a torrefaction temperature of 225 C, the mass loss for lignin was greater than 10% with both pine and switchgrass. The chemical composition of the organosolv lignin is shown in Table 4, which shows that

Table 4
Chemical composition of organosolv lignins used for torrefaction. [a]

Chemical Composition, wt.%	RLP	RLS
Glucan	1.5	0.8
Xylan	1.9	2.3
Mannan	0.0	0.5
Arabinan	0.6	0.0
Galactan	0.5	0.2
Klason lignin	93.6	94.3
Ash (%)	0.65	1.2

[a] Dry, ash-free basis. Single run only.

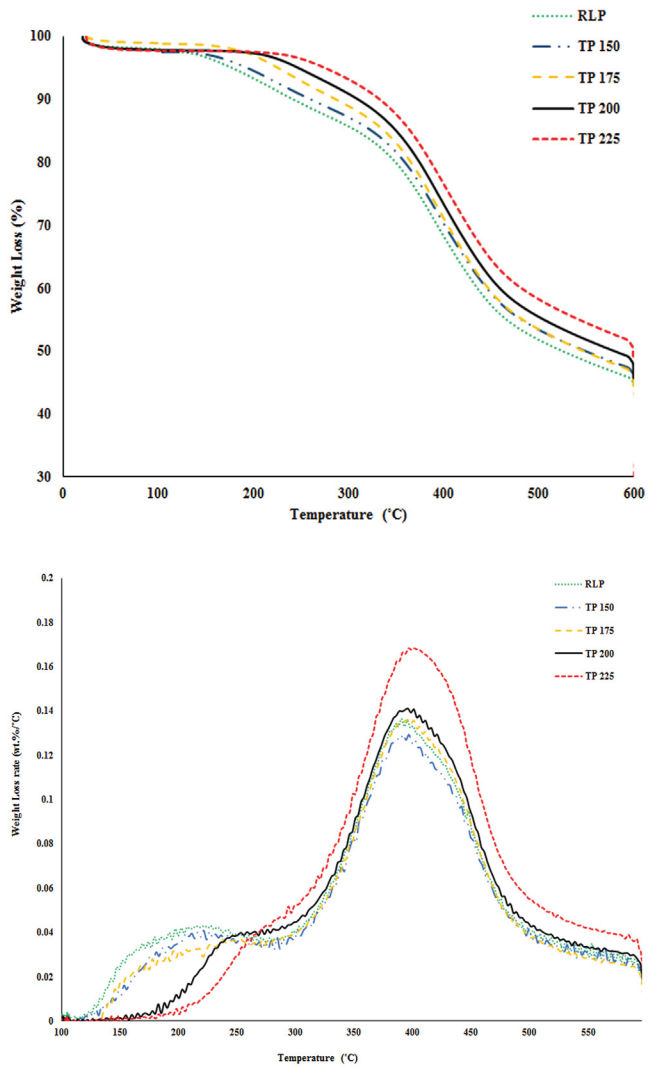

Fig. 2. TG/DTG curves of lignin from pine torrefied at different temperatures.

some residual sugars were present in the lignin even after multiple steps of purification. These results from characterization are similar to the data reported by Srinivasan et al. [19] .

TG and differential TG (DTG) curves obtained for the raw and torrefied lignins are shown in Figs. 2 and 3, which clearly show that the thermal degradation of lignin occurs over a wide temperature range (100 C–600 C). From the DTG curves for pine and switchgrass lignins, the initial/onset temperature of devolatalization (T_i, corresponding to 5% weight loss) can be observed to be increasing with increase in torrefaction temperature. As torrefaction severity increased, the initial peak in the DTG curve (between 120 C–250 C) decreased, which could be attributed to the fact that extensive depolymerization and side-chain splitting of lignin could

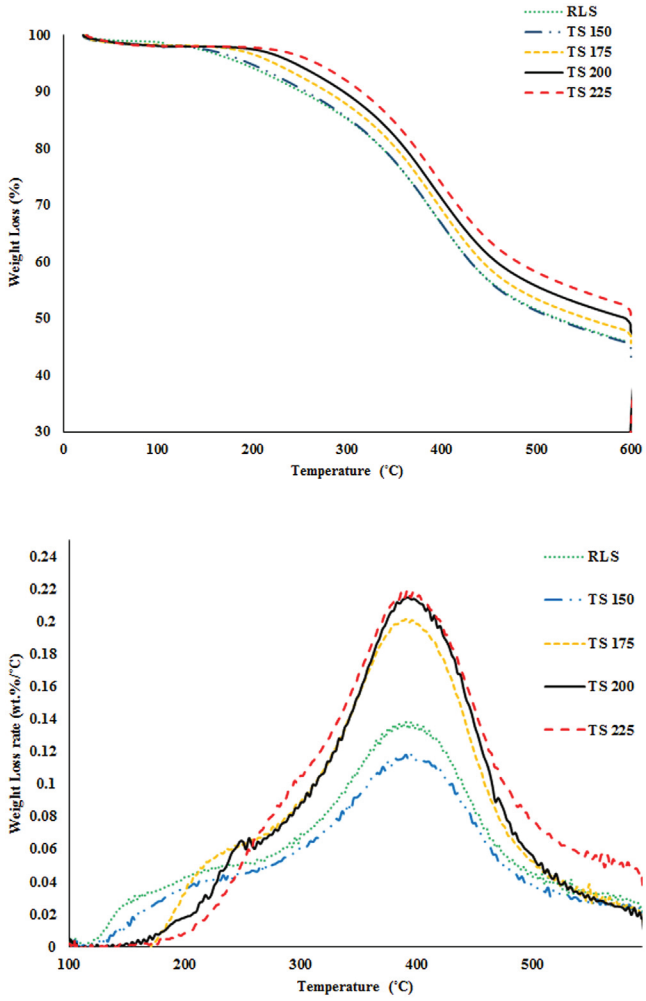

Fig. 3. TG/DTG curves of lignin from switchgrass torrefied at different temperatures.

Table 5
Characteristic parameters from TG/DTG analysis of raw and torrefied lignin.

Feedstock	T_i (C)	DTG_{max} (wt.%/min)	Residue [a] (wt.%)
RLP	182	0.134	44.47
TP 150	193	0.130	45.78
TP 175	227	0.137	45.38
TP 200	248	0.140	47.55
TP 225	276	0.167	50.11
RLS	189	0.138	44.71
TS 150	197	0.120	44.52
TS 175	223	0.200	46.57
TS 200	242	0.214	48.63
TS 225	269	0.220	50.86

[a] Note: The residue (wt.%) is the amount of sample observed at the final temperature of 600 C.

have already taken place during torrefaction at higher temperatures [16] . The characteristic parameters from these curves listed in Table 5 also show that the maximum weight loss rate (DTG_{max}) was significantly higher for lignin from switchgrass when compared to lignin from pine. It should also be noted that torrefaction of lignins at higher temperatures led to an increase in the amount of residues, which increased from 44.47 wt.% to 50.11 wt.% for pine and a similar increase for switchgrass lignin. While these TG/DTG curves give us useful information, they cannot be used as a standalone analytical technique to predict the effect of torrefaction on pyrolysis behavior, since the heating rate employed in this analysis cannot be compared to the heating rates during fast pyrolysis.

3.2. Structural characterization of torrefied lignins

Structural transformations in lignin during torrefaction were characterized by FTIR, ^{13}C CP/MAS NMR and ^{31}P NMR spectroscopy. Further, GPC analysis was performed to observe the change in the molecular weight of the lignins as a result of torrefaction. The FTIR spectra of raw and torrefied lignins from pine and switchgrass are shown in Figs. 4 and 5. The band assignments shown in Table 6 were based on literature data on FTIR analysis of lignins from softwood and herbaceous plants [23] . All the lignin samples showed a broad band at 3420 cm^{-1} (OH stretch) and peaks at 2927 cm^{-1} and 2856 cm^{-1} corresponding to C—H stretching of methyl/methoxyl groups. With increase in torrefaction temperature, there is an increase in the intensity of signals at 1601 cm^{-1} and 1209 cm^{-1} (C—C, C—O and C═O stretch), which could be indicative of aliphatic side chain splitting and polycondensation reactions of lignin [16,24] . Meanwhile, a sharp decrease in the intensity of signals at 1511 cm^{-1} (aromatic skeletal vibrations in lignin), 1459 and 1426 cm^{-1} (methoxy group ($O-CH_3$) of the lignin structure), 1263 cm^{-1} (guaiacyl ring and C—O stretch in lignin) are possible indicators for the demethoxylation, cleavage of β-O-4 linkages in lignin during torrefaction. Further, it can also be seen that bands listed in Table 6 corresponding to guaiacyl and syringyl units in switchgrass appear to also decrease as a result of torrefaction.

The ^{13}C CP/MAS NMR spectra of raw lignin, lignin torrefied at 175 C and 225 C is shown in Fig. 6, with chemical shift (ppm) plotted against the normalized intensity of the signals. The signal with peak between 140 and 160 ppm is assigned to the presence of oxygenated aromatic carbons, 120–140 for aromatic C—C structures and the signal between 50 and 60 ppm is assigned to the methoxyl group in lignin. From Fig. 6, the intensity of the signal at 50–60 ppm can be observed to decrease in the samples torrefied at 225 C, when compared with the raw lignin, which indicates the demethoxylation of lignin during torrefaction. This result correlates well with the product distribution from non-catalytic pyrolysis of these samples discussed in Section 3.3 , as well as with previous studies on biomass torrefaction by Neupane et al. [15] and Zheng et al. [16,17] where the intensity of methoxyl carbons was reported to decrease as a result of torrefaction. Ben et al. [25] and Zheng et al. reported an increase in the intensity of aromatic C—C structures as a result of torrefaction, which was proposed as an indicator of polycondensation reactions occuring in lignin. However in this study, no clear trend can be observed from the signal at 120–140 ppm which is assigned to aromatic C—C structures.

The results from ^{31}P NMR analysis of the raw and torrefied lignins are summarized in Fig. 7. The ^{31}P NMR data shows a clear decrease in the aliphatic OH groups content, which decreases at even mild torrefaction temperatures and severely at the highest torrefaction temperature (225 C). The guaiacyl OH group content also clearly decreases in both pine and switchgrass lignins as a result of a greater degree of demethoxylation reactions at higher torrefaction temperatures. The decrease in the OH group also correlates with the lower oxygen content of the torrefied lignin samples discussed earlier in the elemental composition in Section 3.1 .

The average molecular weights (M_n, M_w) and polydispersity index (PDI) obtained for the lignin samples are summarized in Fig. 8. The polydispersity index is calculated by dividing the weight average molecular weight with the number average molecular weight. Although the ^{13}C NMR data was inconclusive with regards to the occurrence of polycondensation reactions, the number average molecular weight and weight average molecular weights of the lignin samples from GPC analysis could be seen to increase initially with increase in torrefaction temperature, for instance, TLS at 200 C and TLP at 175 C. This indicates the possible formation of condensed aromatic polymers, linked with C—O and C—C bonds. However, it is interesting to note that at the highest tor-

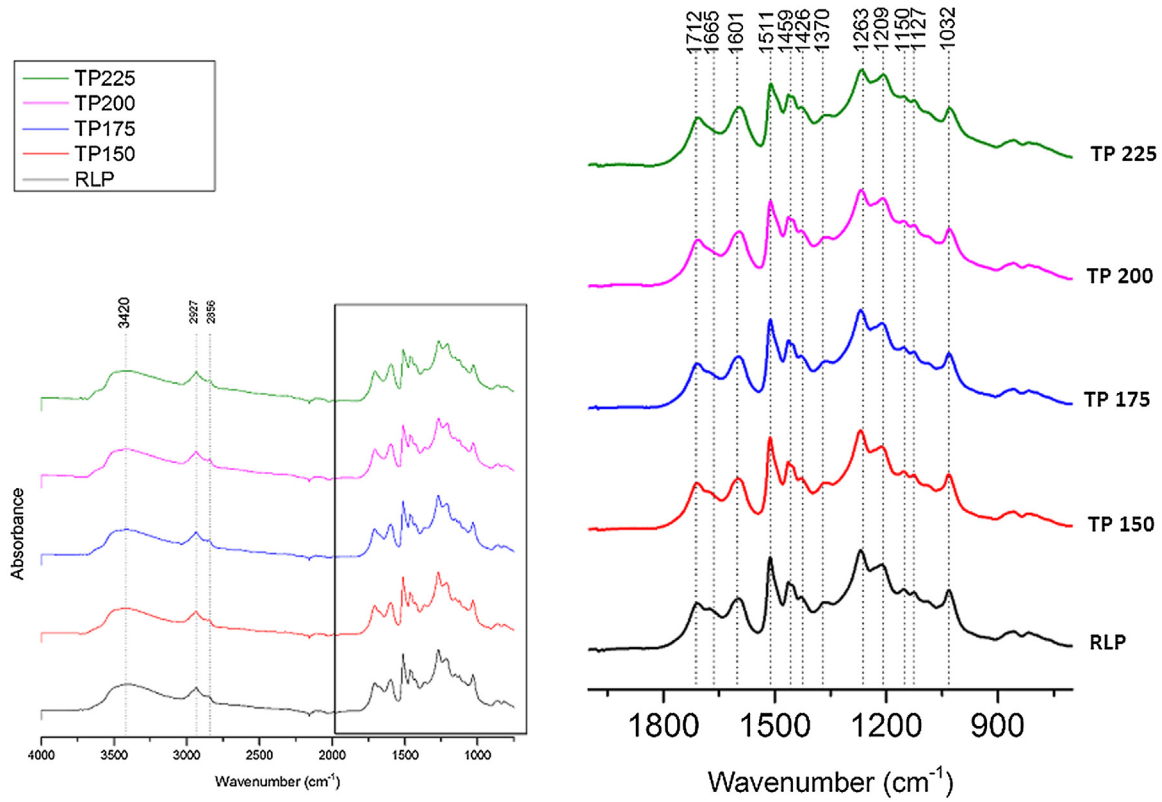

Fig. 4. FTIR spectra of lignin from pine torrefied at different temperatures.

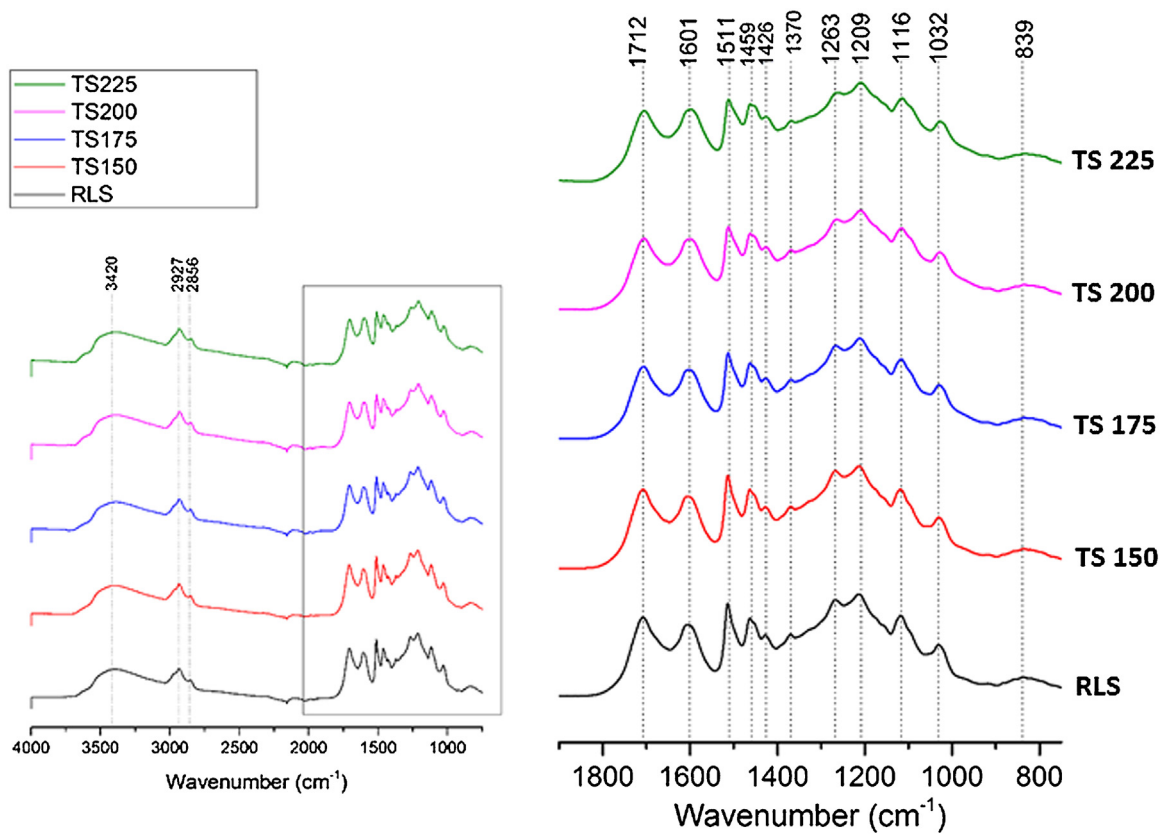

Fig. 5. FTIR spectra of lignin from switchgrass torrefied at different temperatures.

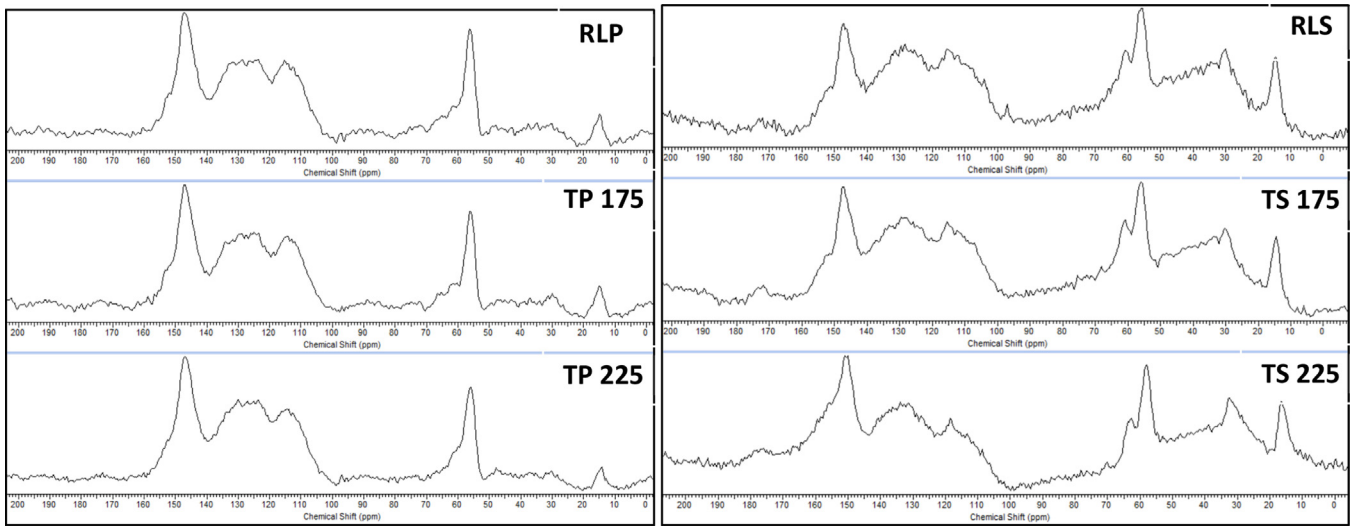

Fig. 6. ^{13}C CP/MAS NMR spectra of lignin from pine and switchgrass.

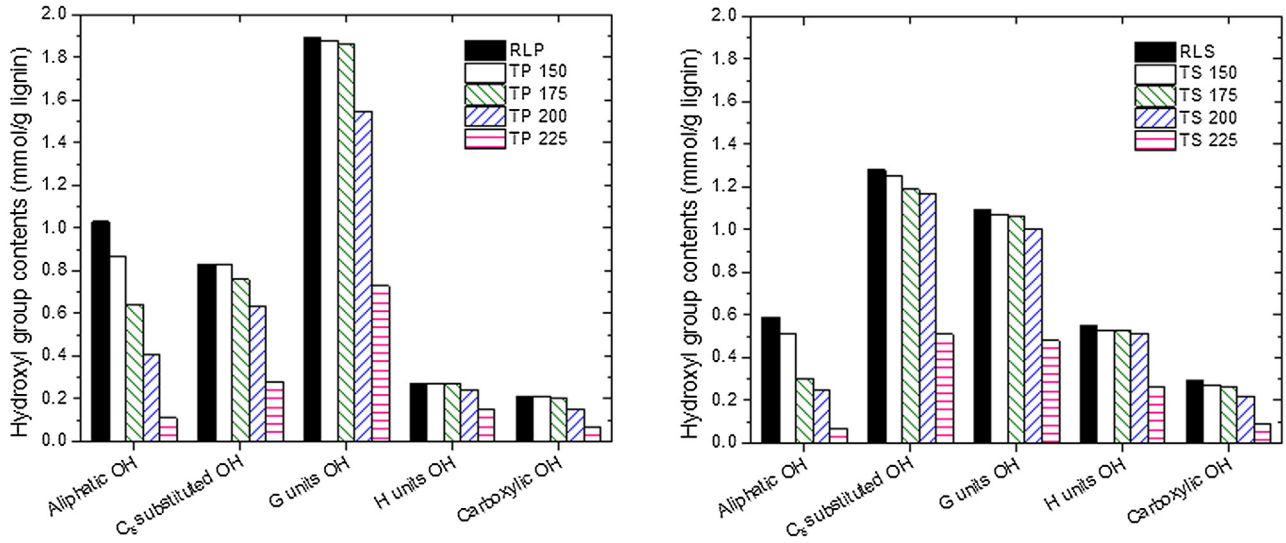

Fig. 7. Hydroxyl group contents from ^{31}P NMR analysis of lignin from pine and switchgrass torrefied at different temperatures.

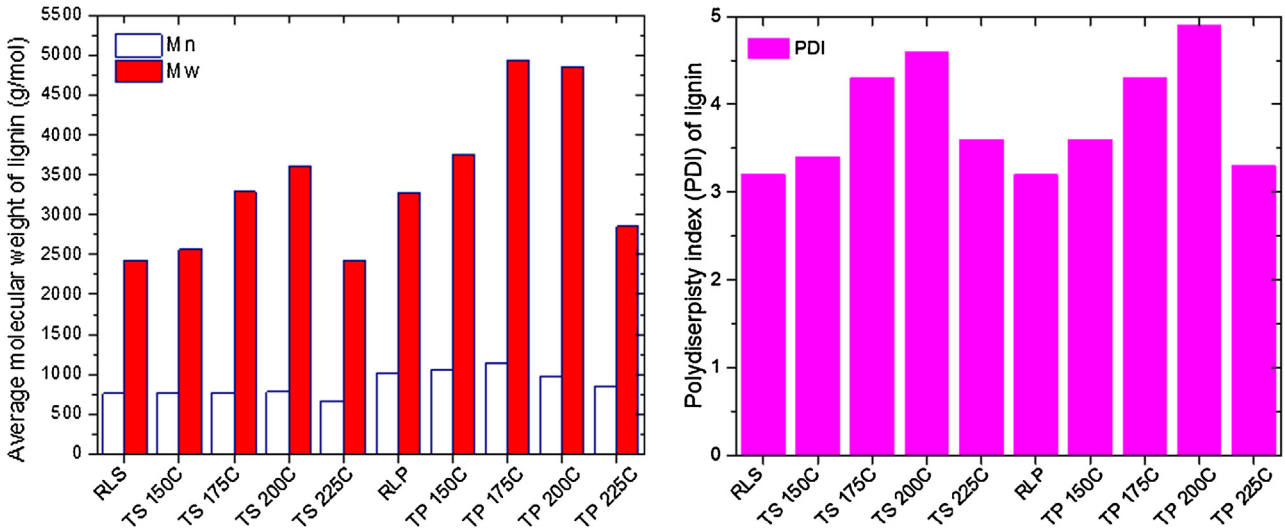

Fig. 8. Average molecular weights (M_n, M_w) and polydispersity index (PDI) from GPC analysis.

Table 6
FTIR analysis of lignin – assignment of main bands between 1800 and 900 cm^{-1}.

Wave number (cm^{-1})	Band origin
3420	O—H stretch
2927	C—H stretch in CH_3 or CH_2 groups
2856	C—H vibration of methyl group of methoxyl
1712	Aromatic skeletal vibration in lignin, C=O stretch (unconjugated)
1665	Aromatic skeletal vibration in lignin, C=O stretch (conjugated)
1601	Aromatic skeletal vibration in lignin, C=O stretch
1511	Aromatic skeletal vibration in lignin
1459,1426	Asymmetry in —CH3 and —CH2 — and the methoxy group (O—CH3) of the lignin structure
1370	Aliphatic C—H stretch in CH_3, phenolic OH
1263	Guaiacyl ring and C—O stretch in lignin
1209	C—C, C—O and C=O stretch
1116–1127	Syringyl ring breathing
1032	Aromatic C—H plane deformation (G + S), C—O deformation in primary alcohols, C=O stretch (unconjugated)

refaction temperature, 225 C, the molecular weights as well as the polydispersity index decreases significantly as the treatment temperature causes further decomposition of these bonds between the condensed polymers.

3.3. Effect of torrefaction temperature on non-catalytic pyrolysis of lignin

To correlate the influence of changes in the structure of lignin and the product distribution from pyrolysis, experiments were performed in a micro-pyrolyzer at 500 C with and without the presence of a catalyst. HZSM-5 zeolite was chosen as the catalyst since it has been the most widely studied and considered unique due to its shape selectivity that suppresses the coke formation, while also maximizing the conversion to aromatic hydrocarbons. Changing the type of catalyst employed during CFP would alter the catalytic upgrading mechanism and ultimately the type of compounds produced. Since we intended to understand the changes due to torrefaction of lignin and compare it to the results from other research groups, we chose the same catalyst in the current study. The major products identified and quantified from the non-catalytic and catalytic pyrolysis of lignin were grouped into four major groups – aromatic hydrocarbons, phenols, guaiacols and syringols. The complete list of compounds is listed in Supplementary information Table S2, where naphthalenes and other polyaromatic hydrocarbons are also included in the aromatic hydrocarbons group. The product distribution from the pyrolysis of lignins from pine and switchgrass is shown in Fig. 9, whereas detailed product yields including the yields of all the compounds quantified are presented in Table 7. In terms of carbon yield, higher torrefaction temperatures appear to cause a significant reduction in the total yield of guaiacols from both pine and switchgrass, whereas the yield of phenols shows an increasing trend with increase in torrefaction temperature. For instance, the yield of guaiacols from raw lignin of pine was 29.8%, which reduced to 10.7% for the sample torrefied at 225 C. Lignin from switchgrass showed a similar trend, albeit to a lesser extent since the yield of guaiacols was lower when compared to pine. Similar results were discussed previously by Adhikari et al. [26] , as well as by Yang et al. [27] investigating the effects of torrefaction on lignin and switchgrass, respectively.

Further, Neupane et al. [15] proposed that torrefaction could enhance demethoxylation and the cleavage of aryl ether linkages in lignin, resulting in the observed decrease in the yield of guaiacols. The results from non-catalytic pyrolysis as well as the structural characterization of torrefied lignins discussed previously seem to support this hypothesis. However, demethoxylation of lignin does not seem to lead to the formation of only phenolic compounds, since the total yield of condensable organic compounds shown in Fig. 9, as well as the overall carbon closure data from Table 7 clearly worsen during the pyrolysis of torrefied lignin samples. The total carbon closure (or balance) reduced from 82.2% (RLP) to 76.9% (TP 225) as a result of torrefying pine, while torrefying switchgrass resulted in overall carbon closure to reduce in a similar fashion. Torrefaction of lignin at higher temperatures also appears to produce an increase in the amount of carbonaceous residues (char) from non-catalytic pyrolysis.

Further, an interesting observation could be made from the yield of syringol (Phenol, 2,6 dimethoxy) in Table 7. While the demethoxylation of G-derivatives from pine (a softwood containing p-hydroxyphenyl and guaiacyl units) appears to be clearly

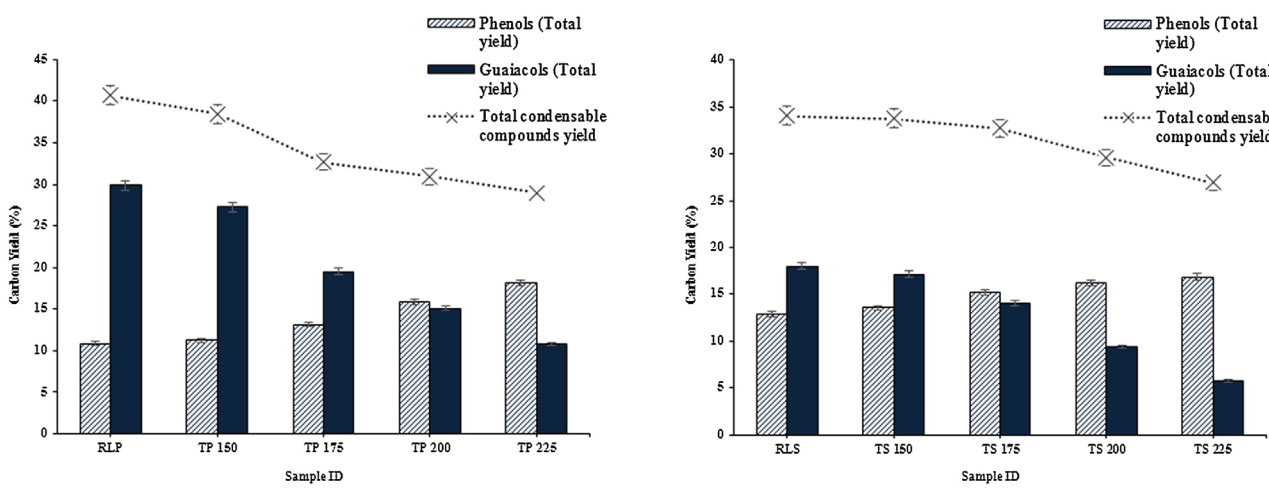

Fig. 9. Product distribution from pyrolysis of lignin from pine and switchgrass torrefied at different temperatures.

Table 7
Product distribution from the non-catalytic pyrolysis of raw and torrefied lignin at 500 C.

Component	Overall Carbon Yield (C%)									
	RLP	TP 150	TP 175	TP 200	TP 225	RLS	TS 150	TS 175	TS 200	TS 225
Condensable compounds	40.7	38.4	32.6	30.9	28.9	34.0	33.7	32.7	29.6	26.9
Char	31.2	32.9	33.3	34.5	35.9	32.1	32.9	33.3	34.2	35.8
Non-condensable gases	10.3	10.9	11.3	12.5	12.1	11.9	11.7	12.2	12.9	13.3
Total Carbon Closure	82.2	82.2	77.2	77.91	76.9	78.0	78.3	78.2	76.7	76.0
Phenols	Overall Carbon Yield (C%)									
Phenol	2.6	3.4	3.2	4.2	4.9	3.1	3.2	4.3	4.1	4.8
Phenol, 2-methyl	1.2	1.1	1.4	1.3	1.4	1.1	1.1	1.2	1.2	1.4
Phenol, 4-methyl	1.1	1.2	2.4	2.8	3.0	2.6	2.7	2.9	3.3	4.1
Phenol, 2,4-dimethyl	0.5	0	0	0	0	1.0	1.1	1.1	1.2	1.4
Phenol, 2,4,6 trimethyl	0	0	0	0	0	0.7	0.6	0.6	0.4	0
Phenol, 3,5 dimethyl	1.6	1.8	1.8	2.2	2.5	0	0	0	0	0
Phenol, 3-ethyl	0.5	0	0	0	0	0	0	0	0	0
Phenol, 4-ethyl	0.7	0.9	1.5	2.1	2.8	1.9	2.3	2.5	3.0	3.2
Catechol	1.1	1.2	1.1	1.2	1.1	1.1	1.1	1.2	1.5	1.3
Phenol, 4-vinyl	0.8	1.2	1.4	1.8	2.3	0	0	0.1	0.4	0.5
Catechol, 4-methyl	0.5	0.2	0	0	0	1.1	0.9	0.9	0.8	0
Total Phenolic Yield	10.8	11.2	13.1	15.7	18.1	12.8	13.5	15.1	16.2	16.8
Guaiacols	Overall Carbon Yield (C%)									
Phenol, 2-methoxy	6.4	5.8	3.1	2.4	1.9	4.6	4.4	3.6	2.5	1.4
Phenol, 2-methoxy-4-methyl	10.7	10.9	7.3	4.6	2.1	6.5	6.1	5.1	3.1	1.2
Phenol, 4-ethyl 2-methoxy	2.5	2.9	2.8	2.9	2.9	1.5	1.6	1.6	1.5	1.5
Eugenol	1.1	0.5	0	0	0	0	0	0	0	0
Iso-eugenol	0.9	0	0	0	0	0	0	0	0	0
Phenol, 2-methoxy 4-vinyl	4.9	4.1	3.5	2.6	1.7	4.1	3.7	2.5	1.6	1.1
Vanillin	3.0	2.8	2.6	2.3	2.0	1.0	1.1	0.9	0.6	0.4
Total Guaiacols Yield	29.8	27.2	19.5	15.1	10.7	17.9	17.1	14	9.3	5.7
Syringols	Overall Carbon Yield (C%)									
Phenol, 2,6 dimethoxy	N/A	N/A	N/A	N/A	N/A	3.1	3.1	3.5	4.0	4.3

N/A: Not available

taking place, the yield of syringol from switchgrass lignin (with two methoxy groups) actually increased from 3.18% (RLS) to 4.3% (TS 225). These results suggest that the degradation behavior of G- and S- units in lignin could be considerably different during torrefaction and pyrolysis. This difference could be a direct result of the inherent difference in the structure of the two types of lignins. While switchgrass contains both syringyl as well as guaiacyl units in the lignin macromolecule, pine being a softwood contains mostly guaiacyl, p-hydroxyphenyl units and no syringyl units. It has been shown by previous studies that the ether bonds linking syringyl units are easier to split than those between guaiacyl units, which would directly explain the increased production of syringol from switchgrass lignin [28,29] . Further, the G-units of lignin undergo condensation and coupling reactions very easily, which results in the formation of stable high molecular weight compounds or char. Since several high molecular weight compounds from lignin pyrolysis as well as GC-undetectable compounds were not quantified and accounted for in our carbon balance, it would explain the reason behind the deteriorating carbon closure and increasing carbonaceous residues with increasing torrefaction severity.

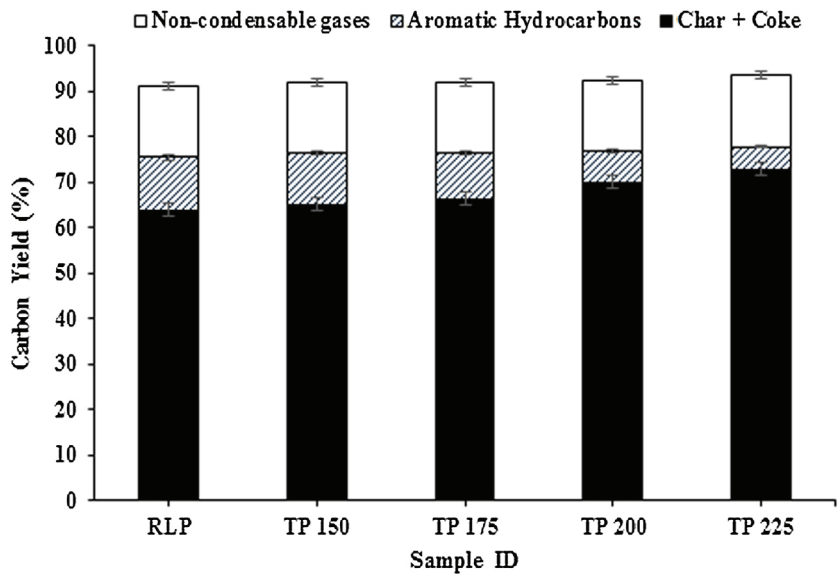

Fig. 10. Product distribution from CFP of raw and torrefied lignin from pine at 500 C.

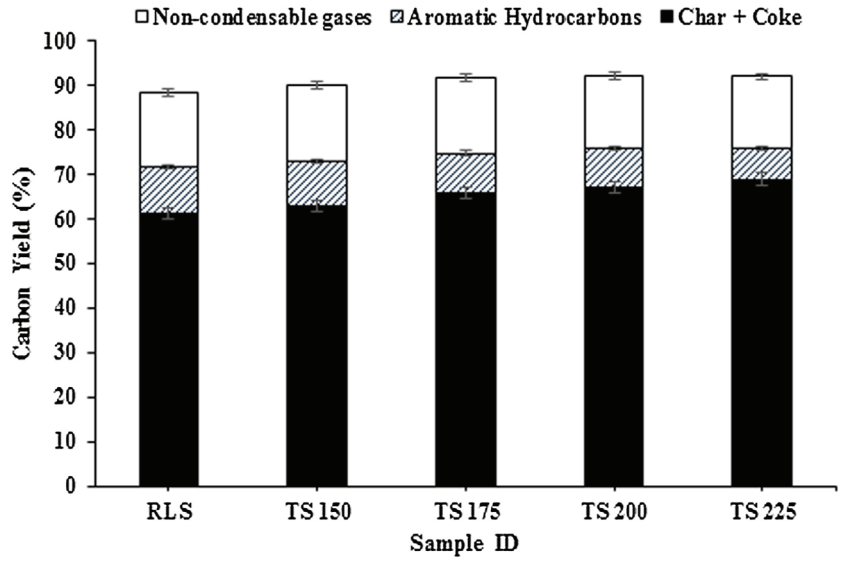

Fig. 11. Product distribution from CFP of raw and torrefied lignin from switchgrass at 500 C.

Finally, it should be noted that while some studies in the past have reported the increased formation of aromatic hydrocarbons from non-catalytic pyrolysis of torrefied biomass/lignin [19,26] , none of the hydrocarbons were detected at any level from the pyrolysis of lignin samples torrefied at any temperature in this study.

3.4. Effect of torrefaction temperature on CFP of lignin

The product distributions from the CFP of raw and torrefied lignins from pine and switchgrass are shown in Figs. 10 and 11, respectively. The group aromatic hydrocarbons contains major compounds that were identified and quantified – benzene, toluene, xylene, ethyl benzene, indane, indene, 2-methyl indene, naphthalene, 1-methyl naphthalene, 2-methyl naphthalene, 2,6 dimethyl naphthalene, phenanthrene, fluorene and anthracene. Although several contemporary studies that investigated the CFP of lignin or biomass at catalyst:biomass ratios similar to this study have reported the formation of small amounts of oxygenated compounds (<3%) such as phenols or guaiacols, those compounds were not identified in this study which could be a result of uniform sample preparation (catalyst:biomass mixture) [16,19,26] .

As shown in Fig. 10, the yield of aromatic hydrocarbons from raw lignin of pine was 11.6%, which decreased to 4.9% at the maximum torrefaction temperature of 225 C. The decrease in the yield of aromatic hydrocarbons was accompanied by a corresponding increase in the yield of carbonaceous residues (coke + char), which increased from 63.9% to 72.8%. A similar trend can also be observed clearly in the product distribution from CFP of torrefied switchgrass lignin from Fig. 11. Zheng et al. proposed that the increase in carbonaceous residues from CFP could be related to the increasing polycondensation of lignin samples torrefied at higher temperatures [16] . Further, several studies including the work on CFP of

Table 8
Product distribution from CFP of raw and torrefied lignin at 500 C.

Component	Overall Carbon Yield (C%)									
	RLP	TP 150	TP 175	TP 200	TP 225	RLS	TS 150	TS 175	TS 200	TS 225
CO	5.9	5.5	5.7	5.0	4.8	6.9	6.6	6.4	5.8	5.1
CO_2	5.4	5.7	6.1	7.6	8.9	6.7	6.8	7.3	7.9	8.2
Char + Coke	63.9	65.1	66.3	69.9	72.8	61.3	63.1	65.7	67.1	68.9
Char [a]	31.2	32.9	33.3	34.5	35.9	32.1	31.9	32.2	32.4	32.8
Coke [b]	32.7	32.2	33	35.4	36.9	29.2	31.2	33.5	34.7	36.1
Aromatic hydrocarbons	11.6	11.3	10.1	6.8	4.9	10.4	9.9	9.1	8.6	7.1
Olefins (C2-C4)	4.1	4.1	3.4	2.8	1.93	3.9	3.02	2.89	2.7	2.5
Non-condensable gases	15.5	15.4	15.3	15.5	15.7	17.5	16.5	16.7	16.5	15.9
Oxygenated Compounds	0	0	0	0	0	0	0	0	0	0
Total Carbon Closure	91.0	91.8	91.7	92.2	93.4	89.2	89.5	91.5	92.2	91.9
	Aromatics Selectivity (%)									
Benzene	13.9	14.1	14.8	15.6	16.1	11.3	11.9	12.6	16.3	15.8
Toluene	16.8	17.9	18.6	19.5	20.4	20.2	20.9	22.1	21.8	23.5
Xylene	18.9	19.4	22.9	23.8	24.9	17.8	17.4	18.2	18.7	20.1
BTX Selectivity	49.6	51.4	56.3	58.9	61.4	49.3	50.2	52.9	56.8	59.4
Ethyl Benzene	0.9	0.9	0.2	0	0	0	0	0	0	0
C9 Aromatics	13.0	12.9	12.0	11.1	9.7	14.1	14.8	14.0	13.5	12.9
C10+ Aromatics	36.3	34.7	31.4	29.8	28.8	36.6	34.9	33	29.6	27.6
Naphthalenes	26.7	25.6	23.2	22.1	21.3	29.4	27.6	26.1	23.9	22.1
Fluorene, Anthracene	9.5	9.1	8.1	7.7	7.4	7.2	7.34	6.9	5.7	5.5

Note: Std. deviation was negligible and is not shown since the error was within 5% for all the results.
C9 Aromatics include indane, indenes and alkyl benzenes.
[a] Result from non-catalytic experiments performed.
[b] Difference between char+coke from CFP experiment and char yield from non-catalytic.

various types of lignins by Mullen et al. [13] and the CFP conversion of model compounds for lignin (phenol, anisole) by Thilakaratne et al. [30] have suggested that simple phenols are more likely to lead to the formation of coke rather than to an increased yield of aromatic hydrocarbons. These results shed more light on the product distribution from CFP of torrefied lignins from pine and switchgrass since the higher yield of phenols at higher temperatures of torrefaction has clearly caused the increased formation of coke. Finally, the selectivity of BTX compounds shown in Table 8 could be seen to improve with an increase in torrefaction temperature, from 49.7% from RLP to 61.5% from TP 225. A very similar increase can also be seen in the selectivity of BTX compounds produced from CFP of torrefied lignins from switchgrass, which is primarily due to the loss in yield of some poly aromatic hydrocarbons such as naphthalenes, fluorene and anthracene with increase in torrefaction temperature. These polyaromatics are primarily formed from the reaction of olefins with the phenyl radical and hence the decrease in their yields as a result of torrefaction is expected. However, looking into any change in selectivity has very little practical significance when the carbon yield of the desired product (aromatic hydrocarbons) is reduced significantly as a result of torrefaction.

4. Conclusions

Organosolv lignin extracted from pine and switchgrass was subjected to torrefaction at various temperatures (150 ⁰C, 175 ⁰C, 200 ⁰C and 225 ⁰C) in order to understand the effect of torrefaction on structural changes in the lignin macromolecule. FTIR and NMR spectroscopy of torrefied lignins shed light on the enhanced cleavage of aryl ether linkages in lignin and the demethoxylation/polycondensation of guaiacyl lignin. Non-catalytic pyrolysis of the torrefied lignins confirmed the results from previous studies on biomass torrefaction, resulting in a significant shift in the pyrolysis product distribution towards producing more phenols and carbonaceous residues. The behavior of guaiacyl and syringyl lignin units during torrefaction was also shown to be significantly different. However, in-situ CFP experiments showed that torrefaction negatively impacts lignin resulting in a significant loss in the yield of aromatic hydrocarbons (11.6% to 4.9% in pine; 10.4% to 7.1% in switchgrass).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found.

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