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Heating rate and temperature effects on pyrolysis products from live wildland fuels☆

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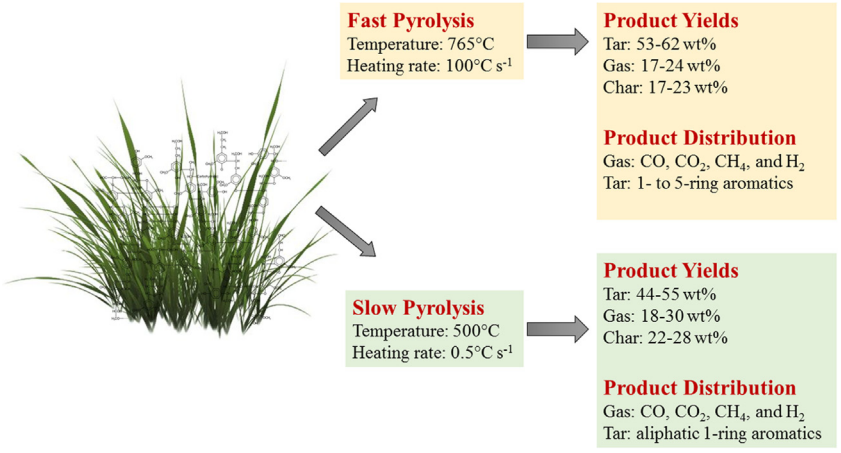
GRAPHICAL ABSTRACT



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ABSTRACT

Wildland fire, which includes both planned (prescribed fire) and unplanned (wildfire) fires, is an important component of many ecosystems. During wildland fires, low heating rate pyrolysis (slow pyrolysis) occurs during preheating and/or smoldering of plant material. High heating rate pyrolysis (fast pyrolysis) exists in the flame region. Pyrolysis temperature and heating rate play important roles on the yields and the compositions of pyrolysis products. In this work, the effects of pyrolysis temperature and heating rate on the yields and the compositions of pyrolysis products from 14 plant species native to the forests of the southern United States are shown. The slow pyrolysis experiments were performed at a low heating rate of 0.5 °C s^{-1} and an operating temperature of 500 °C. However, the fast pyrolysis experiments were operated at a high heating rate of 180 °C s^{-1} and a temperature of 765 °C. The yields and compositions of the pyrolysis products during the slow and fast pyrolysis experiments were analyzed in detail. The results showed that the average tar yield for all plant species (live and dead) was 58 wt% on a dry-ash free (daf) basis for the fast pyrolysis experiments compared to 49 wt% (daf) for the slow pyrolysis experiments, an increase of 9 wt%. The average gas yields for the slow and fast pyrolysis of the plants were 20 and 22 wt% (daf), respectively. The average volatile yield increased from 69 wt% (daf) at the low heating rate experiments to 80 wt% (daf) for the high heating rate experiments. The major light gas species for both the slow and fast pyrolysis experiments (wt% basis) were CO, CO_2, CH_4, and H_2,

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with higher yields of CO observed in the high heating rate experiments and higher yields of CO_2 in the slow pyrolysis experiments. The slow pyrolysis experiments led to formation of aliphatic and 1-ring aromatic compounds with large number of attachments on their rings, such as phenol, 1,2-benzenediol, 2-methoxy phenol, etc. In the fast pyrolysis experiments, phenol was still one of the major products. However, in contrast with the slow pyrolysis experiments, 1- to 5-ring aromatic compounds with very few attachments, such as fluorene, anthracene, phenanthrene, fluoranthene, pyrene, etc. were major tar compounds during the fast pyrolysis experiments.

1. Introduction

It is well known that heating rate and temperature affect pyrolysis yields and product distributions of solid fuels such as coal and biomass [1–14]. Increases in heating rate and temperature enhance gas and tar yields, with a concurrent decrease in char yields [15,16]. As temperatures are increased, eventually tar cracking is observed and additional solid pyrolysis reactions occur [17,18]. Pyrolysis can be classified into three groups depending on heating rate and temperature, as shown in Table 1 [19].

Pyrolysis of wood and other types of biomass such as agricultural wastes is commonly related to the constituent composition (i.e., hemicellulose, cellulose, and lignin). Temperature ranges of slow pyrolysis of hemicellulose, cellulose, and lignin have been shown to be 180–240, 230–310, and 300–500 °C, respectively, depending on the heating rate [20].

Pyrolysis of live vegetation is of interest when modeling wildland fires. Live vegetation consists of not only hemicellulose, cellulose, and lignin, but many other compounds such as non-structural carbohydrates, fats, and other components [21–23]. It is not clear how changes in heating rate and temperature affect the pyrolysis behavior of live vegetation. Slow pyrolysis of wildland fuels can occur during preheating by a fire, or during smoldering. For this study, the heat fluxes were selected to imitate fast pyrolysis of live plant species under the convective heat flux of approximately 100 kW m^{-2} typical of wildland brush fires [24].

Lin, et al. [25] has reported that by increasing pyrolysis temperature and heating rate, char yield decreases, gas yield increases, and tar yield increases until it reaches its maximum value and then decreases due to the decomposition of tar compounds to light gases. Fast pyrolysis, which occurs at higher heating rates and lower residence time, may lead to higher gas and tar yields, while slow pyrolysis leads to higher char yield [15,16]. Higher yield of volatiles in fast pyrolysis is caused by further cracking of char as well as decomposition of tar compounds which undergo secondary reactions [17,18]. In another study, Sussott [26] measured the char yields at 500 °C of foliage, wood, small stems, and bark at heating rates from 20 °C min^{-1} to about 1000 °C min^{-1}. His samples were freeze-dried and ground to pass through a 20-mesh screen (0.84 mm) before pyrolysis. Sussott's results showed little difference in char yield as heating rate was increased. However, Zhao, et al. [27] studied the effects of temperature and heating rate on tar and char yields from the pyrolysis of rapeseed stem. Zhao's results indicated that by increasing the heating rate starting at 1 °C min^{-1}, char yield increased until it reached its maximum value at the heating rate of 5 °C min^{-1}, then char yield decreased continuously at higher heating rates. Other studies have shown that higher heating rates favor higher tar yield and lower char yield, higher temperatures provide higher light gas yield, but lower temperatures and heating rates favor higher char yield [28–30].

Results of pyrolysis of 14 live plant species from the southern United States under fast heating conditions [31] and slow heating conditions were previously published [32]. In these experiments, all samples were left intact with no grinding or crushing. This paper presents a detailed comparison of the slow and fast pyrolysis data, along with results of additional experiments, with the goal of detailing the effects of heating rate and temperature on pyrolysis products.

2. Material and methods

2.1. Fuels tested

The plant species as listed in Table 2 were nursery grown in Florida. Live potted plants were then express-mailed to the combustion laboratory at Brigham Young University (BYU). Two of the plant species were grasses (little bluestem grass and wiregrass), 9 were shrub species, and others were tree species. Longleaf pine litter (i.e., pine straw) was also studied and compared with the live and 1-week old dead longleaf pine foliage data to investigate the effects of aging on the composition of pyrolysis products. Proximate and ultimate analyses of the live and dead species, along with physical properties, were published previously [31,32]. Sample moisture content was measured before each experiment.

2.2. Experimental setup and procedure

A pyrolyzer apparatus [32–34] was used for the low heating rate (slow pyrolysis) experiments in order to collect sufficient tar for analysis. A flat-flame burner apparatus [31,35] was used for the high heating rate (fast pyrolysis) experiments. The discussion in this work is based mainly on pyrolysis of live plants.

2.2.1. Slow pyrolysis experiments

The pyrolyzer apparatus (as shown in Fig. 1) provided slow pyrolysis at 0.5 °C s^{-1} until reaching a gas phase temperature of 500 °C, and then kept at this temperature for up to an hour until no further gas generation was observed [32,34]. N_2 was used as a sweep gas to provide an oxygen-free environment. The pyrolysis products were collected and then analyzed using a combined gas chromatograph and mass spectrometer (GC–MS) for analysis of tar and a gas chromatograph with a thermal conductivity detector (GC-TCD) for analysis of light gases. Furthermore, another study was performed on one plant species (longleaf pine litter) to separate the effects of temperature and heating rate. Longleaf pine litter was pyrolyzed at 0.5 °C s^{-1} to a maximum temperature of 765 °C to compare with the data from the pyrolyzer and the FFB apparatus.

2.2.2. Fast pyrolysis experiments

A flat-flame burner (FFB) apparatus (as shown in Fig. 2) was used to provide an approximate heating rate of 180 °C s^{-1} and a gas temperature of 765 °C [31,35]. The FFB was operated in a fuel-rich mode (equivalence ratio: $\Phi = 1.13$) to provide an oxygen-free environment (i.e., no sample combustion). Samples were heated convectively by the post-flame gases (CO_2, H_2O, and CO). Post-flame gases were analyzed with the GC-TCD in order to ensure an oxygen-free environment. The

Table 1
Pyrolysis classification.

Pyrolysis type	Heating rate (°C s^{-1})	Temperature (°C)	Gas and solid residence time
Slow	0.1–1	300–500	more than 30 min
Fast	1–100	500–900	10–20 s
Flash	> 1000	500–900	1 s

Table 2
List of plants used in pyrolysis experiments.

Scientific name	Common name	Growth form
Aristida stricta Michx.	Wiregrass	Grass
Ilex glabra (L.) A. Gray	Inkberry	Shrub
Ilex vomitoria Aiton 'Schelling Dwarf'	Yaupon	Shrub
Lyonia lucida (Lam.) K. Koch	Fetterbush	Shrub
Morella cerifera (L.) Small	Wax myrtle	Shrub
Persea palustris (Raf.) Sarg.	Swamp bay	Shrub
Pinus palustris Mill.	Longleaf pine foliage	Tree
Pinus palustris Mill.	Longleaf pine litter	Tree
Quercus nigra L.	Water oak	Tree
Quercus virginiana Mill.	Live oak	Tree
Sabal minor (Jacq.) Pers.	Dwarf palmetto	Shrub
Schizachyrium scoparium (Michx.) Nash	Little bluestem	Grass
Serenoa repens (W. Bartram) Small	Saw palmetto	Shrub
Vaccinium arboreum Marshall	Sparkleberry	Shrub
Vaccinium darrowii Camp "Rosa's Blush"	Darrow's blueberry	Shrub

products were collected and analyzed off-line using GC-TCD (for light gases) and GC–MS (for tars) using the same procedure as for the pyrolyzer. It should be noted that the gas residence time in the transfer line of both the pyrolyzer and the FFB apparatus was estimated to be approximately 100 ms [35].

2.3. Statistical analysis

All the results which have been presented in this study are the average of three experiments. The error bars in the figures represent the ± 95% confidence intervals for three experiments (as shown in Equation (1). The average values ($\bar{x}$) and the standard deviations (s) for three replications were first calculated. The t-value, which is a function of the number of replications and the confidence interval, was found to be equal to 2.92 for three replications (n = 3) and 95% confidence intervals (α = 1–0.95 then α = 0.05) using the t-value table [36]. The confidence values about the mean were then calculated as follows:

$$\mu = \bar{x} \pm t \bullet \left(\frac{s}{\sqrt{n}}\right) \quad (1)$$

The ANOVA (Analysis of Variance) data analysis tool in Microsoft Excel 2017 was used to calculate the p-values for the statistical analysis. This statistical analysis technique can be used to determine whether the differences between the means of three or more independent groups are statistically significant. The null hypothesis is that the means of the independent groups are the same. The null hypothesis is rejected if the p-value is less than 0.05. If the p-value is found to be in the range 0–0.01, then it is considered to be convincing evidence that the null hypothesis should be rejected and the difference between the means of the independent groups is statistically significant. If the p-value is between 0.01 and 0.05, there is moderate evidence of difference between the means of the independent groups. A p-value between 0.05 and 0.1 indicates that there is a difference between the means, however, it is inconclusive. If the p-value is greater than 0.1, the difference between the means is not significant [36]. This method of p-value interpretation has been used in this study for the statistical analysis.

3. Results and discussion

3.1. Pyrolysis product yields

Figs. 3–5 show comparisons of the gas, tar, and char yields obtained from the slow and fast pyrolysis of live plant species. As shown in Fig. 3, the gas yield from the fast pyrolysis was always higher for each species. The results from the ANOVA statistical analysis indicate that there was a suggestive, but inconclusive evidence of a difference between the means of light gas yields from the slow and fast pyrolysis experiments (p-value = 0.05). Saw palmetto showed the highest gas yield during both slow and fast pyrolysis experiments (24 and 25 wt%, respectively). Swamp bay showed the largest difference (2.3 wt%) between the gas yields from slow and fast pyrolysis experiments. No correlation was found between light gas yield and elemental composition of the unreacted plant species.

Higher tar yield and lower char yield were obtained for all plant species from the fast pyrolysis experiments, as shown in Figs. 4 and 5. In contrast with the light gas yield results, for most plant species, the tar and char yields measured for the two heating rates showed non-overlapping confidence intervals, indicating that there was convincing evidence of differences between the results from slow and fast pyrolysis experiments (tar p-value = 4×10^{-8}, char p-value = 3×10^{-13}).

Dwarf palmetto showed the highest tar yield during both slow and fast pyrolysis experiments (54 and 62 wt%, respectively). Wax myrtle showed the largest difference (11 wt%) between the tar yields from slow and fast pyrolysis experiments. Live oak and sparkleberry showed the highest char yield (34 wt%) in slow pyrolysis experiments, followed by wax myrtle (33 wt%) and water oak (32 wt%). These plant species also had the highest char yield during fast pyrolysis experiments. Like the tar yield results, wax myrtle showed there was convincing evidence of difference between the char yields (12 wt%) from slow and fast pyrolysis experiments.

Figs. 4 and 5 indicate that the plants from the same genus (i.e., (i) live oak and water oak, (ii) inkberry and yaupon, and (iii) sparkleberry and Darrow's blueberry) showed very similar tar and char yields during both slow and fast pyrolysis experiments.

The pyrolysis product yield data from Figs. 3–5 are summarized in Table 3. The tar yields were 8–9 wt% higher in the fast pyrolysis experiments, while the light gas yields were only 2–3 wt% higher in the high heating rate experiments. The increased tar and light gas yields at high heating rates resulted in lower char yields by 10–12 wt%. The average total volatile yields (i.e., tar plus light gas) for all live plant

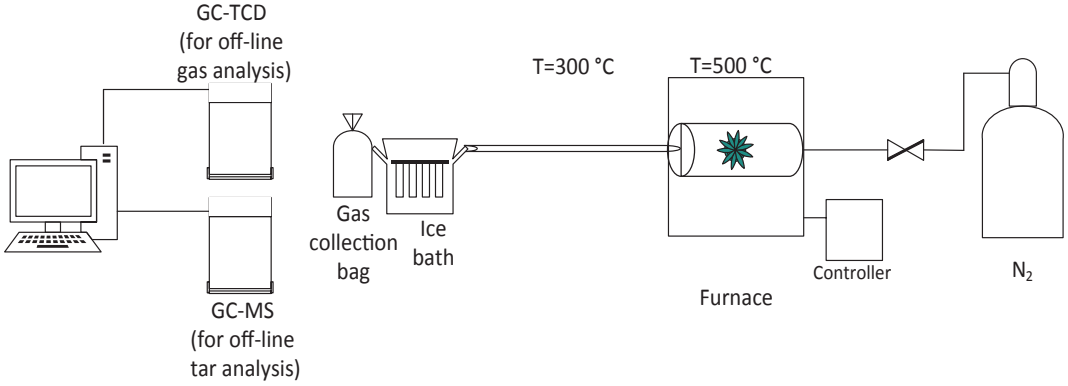

Fig. 1. Pyrolyzer apparatus. Taken from [32].

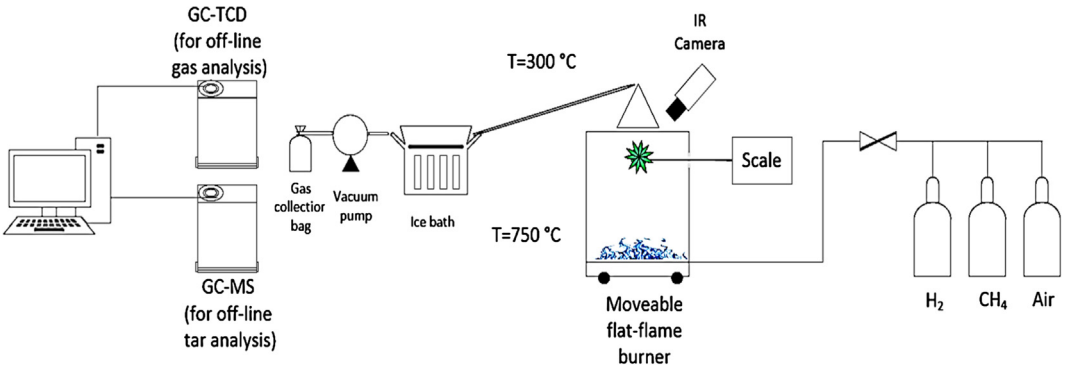

Fig. 2. Flat-flame burner apparatus. Taken from [31].

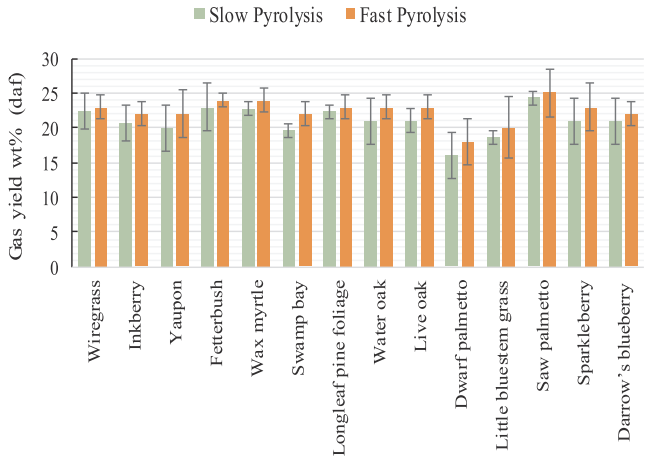

Fig. 3. Gas yield of live plant species on a dry, ash free (daf) basis.

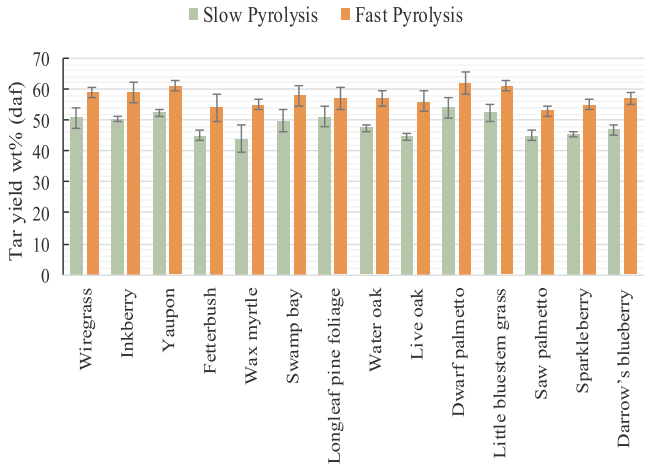

Fig. 4. Tar yield of live plant species on a dry, ash free (daf) basis.

species, increased from 69 wt% in the slow pyrolysis to 81 wt% for the fast pyrolysis.

These results indicate that heating rate and operating temperature had a significant impact on the yields of pyrolysis products, especially the tar and char yields. For the fast pyrolysis experiments, the increased heating rate was expected to increase the tar yield. The increased temperature was expected to first increase and then decrease the tar yield, with increased gas yield due to tar cracking, based on observations of biomass tar in the literature [15,17,18,37,38]. In addition to the heating rate and temperature, residence time of the fuel in the reaction zone also has a significant effect on the yields of pyrolysis products [39]. However, the effect of the residence time was not included

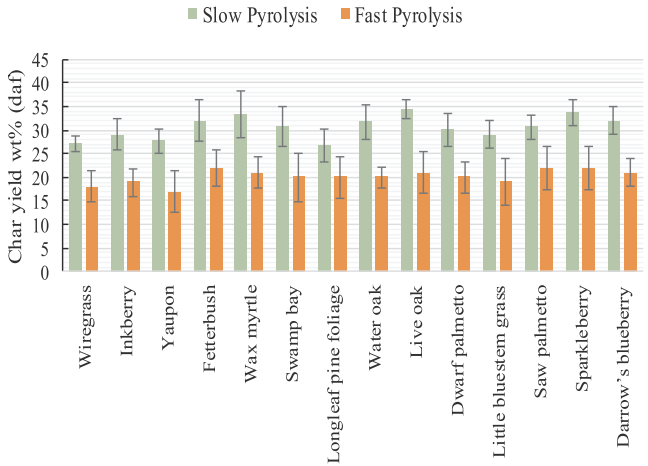

Fig. 5. Char yield of live plant species on a dry, ash free (daf) basis.

Table 3
Ranges of the pyrolysis product yields from live plants.[a]

Heating Rate	Tar Yield[a]	Light Gas Yield[a]	Char Yield[a]
0.5 °C s^{-1}	44–54	16–24	27–34
180 °C s^{-1}	53–62	18–25	17–22

[a] wt% on a dry, ash-free basis.

in the present study. Increasing the residence time generally enhances the gas yield, which is caused by the decomposition of tar and char. The effect of residence time on the tar yield may be much stronger than that of the char yield due to secondary reactions of tar [40].

The differences shown in pyrolysis product yields in the data above may have been due to either the difference in heating rate or due to the difference in final temperature achieved. A study was therefore performed on one plant species to separate the effects of temperature and heating rate. Longleaf pine litter was pyrolyzed at 0.5 °C s^{-1} to a maximum temperature of 765 °C to compare with the data from the pyrolyzer and the FFB apparatus. The yields of pyrolysis products from the longleaf pine litter for three different pyrolysis conditions are shown in Fig. 6. By keeping the heating rate constant (0.5 °C s^{-1}) and increasing the pyrolysis temperature from 500 °C to 765 °C, char yield decreased from 27 to 25 wt%, indicating a 2 wt% increase in the volatile yield. In addition, tar yield decreased by 2 wt% at the higher temperature (with low heating rate) due to the secondary reactions of tar compounds to increase the light gas yield. The increase in temperature at this low heating rate increased the CO yield by 2.6 wt%, with smaller increases in CO_2, CH_4, and H_2. In contrast, by keeping the pyrolysis temperature constant at 765 °C, and increasing the heating rate from 0.5 °C s^{-1} to 180 °C s^{-1}, char yield decreased noticeably from

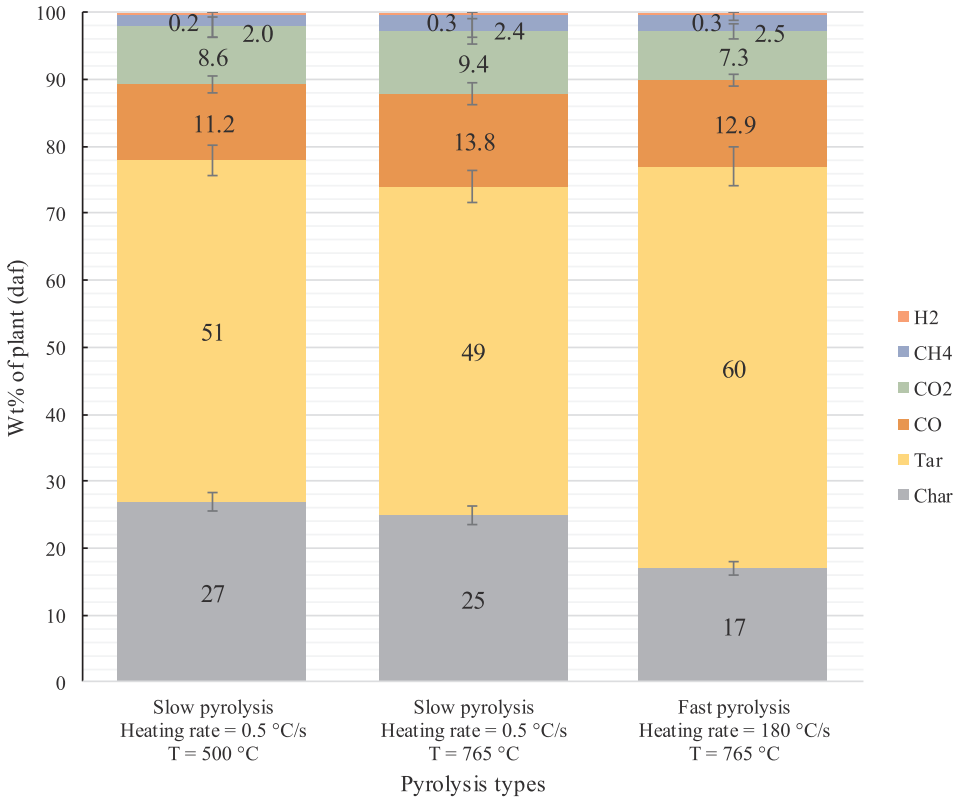

Fig. 6. Pyrolysis product yields from pyrolysis of longleaf pine litter.

25 to 17 wt%, tar yield increased from 49 to 60 wt%, and light gas yield decreased from 26 to 23 wt%. The increase in heating rate at 765 °C changed the yield of CO_2 more than the other light gas species. These results seem to indicate that the heating rate affects tar yield more than the temperature, at least for this plant species.

3.2. Light gas analysis

The analysis of yield of light gases; CO, CO_2, CH_4, and H_2, during slow and fast pyrolysis of all live plant species are shown in Figs. 7–10. To correlate with the light gas yields, which were on a mass basis, the yields of the light gases are presented as a wt% of gas species relative to the total mass of dry gases.

The results show that for both slow and fast pyrolysis experiments, CO was the main component in the light gases on a wt% dry basis, followed by CO_2, CH_4, and H_2. All other gas species, such as C_2H_6 and C_3H_8, were below the detection limit of the GC-TCD instrument (500 ppm). The statistical analysis indicates that there was convincing evidence of a difference between the yields of all light gas species comparing slow vs. fast pyrolysis of live plant species (CO p-value = 4×10^{-8}, CO_2 p-value = 4×10^{-10}, CH_4 p-value = 5×10^{-17}, and H_2 p-value = 1×10^{-3}).

As shown in Fig. 7, the fast pyrolysis experiments compared with the slow pyrolysis experiments, led to a higher wt% of CO for all plant species. Longleaf pine foliage showed the highest yield of CO (58 wt%) for the slow pyrolysis experiments. Saw palmetto had the highest yield of CO (63 wt%) for the fast pyrolysis experiments. Large differences in the compositions of light gases were observed at the different heating rates. Dwarf palmetto showed the largest difference in CO yield (13 wt %) between the slow and fast pyrolysis experiments. The plant species with the second largest difference in CO yield was saw palmetto (11 wt %). Decarbonylation reaction at high heating rates and temperatures is thought to form high yields of CO during pyrolysis of plants [41,42]. The variation in CO yields due to plant species was larger in the slow heating experiments than in the high heating rate experiments. A CO yield of 59 wt% would pass through all of the error bars in the high heating rate data, but no common CO yield would pass through all of the error bars for the slow heating rate data. Furthermore, the results show that the plants from the same genus (e.g., yaupon and inkberry or live oak and water oak) had similar behavior during pyrolysis.

The light gas with the second highest yield was CO_2 (see Fig. 8). The results indicate that by increasing the pyrolysis temperature and the heating rate, CO_2 formation shows a different trend than CO; higher CO_2 yields were obtained from the slow pyrolysis of plant species. The average CO/CO_2 ratio increased from 1.29 (slow pyrolysis experiments) to 1.92 (fast pyrolysis experiments) by increasing the pyrolysis temperature and the heating rate. At high temperatures, CO_2 is thought to be mainly formed by the thermal decomposition of lignin [41].

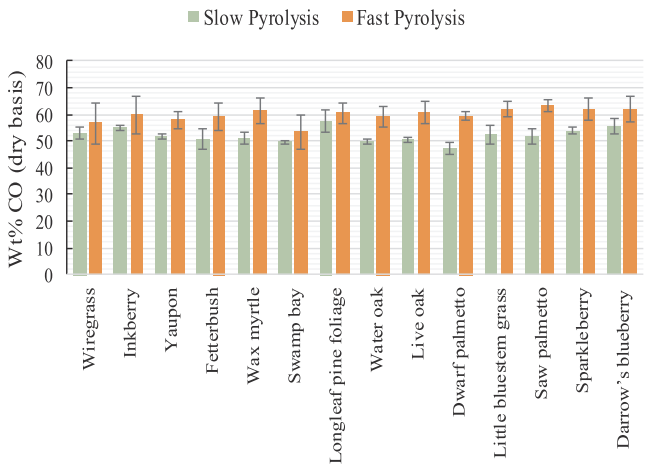

Fig. 7. The yield of CO wt% (dry gas basis) obtained from pyrolysis of live plant species.

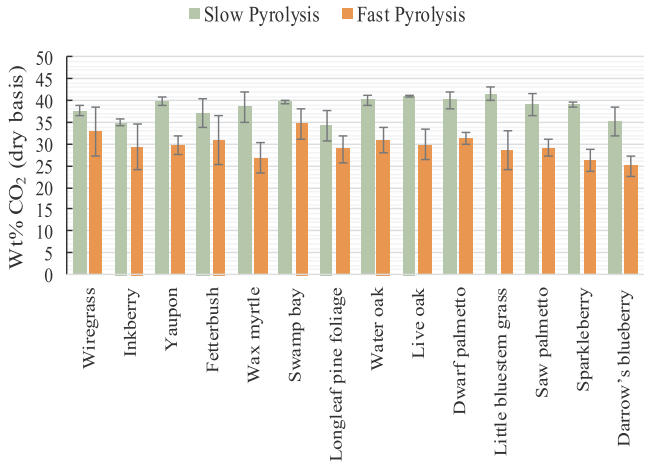

Fig. 8. The yield of CO_2 wt% (dry basis) obtained from pyrolysis of live plant species.

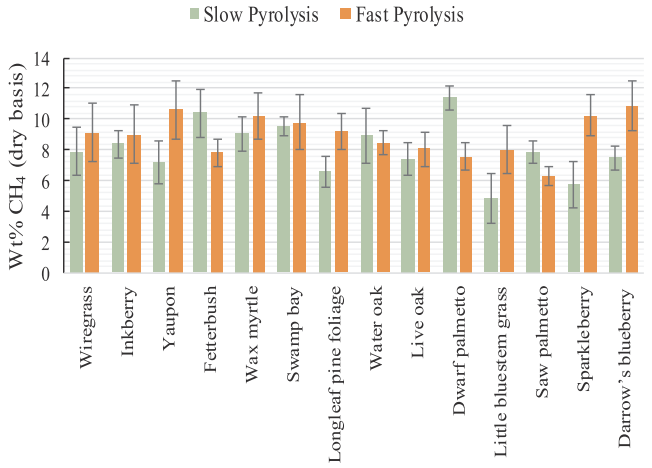

Fig. 9. The yield of CH_4 wt% (dry basis) obtained from pyrolysis of live plant species.

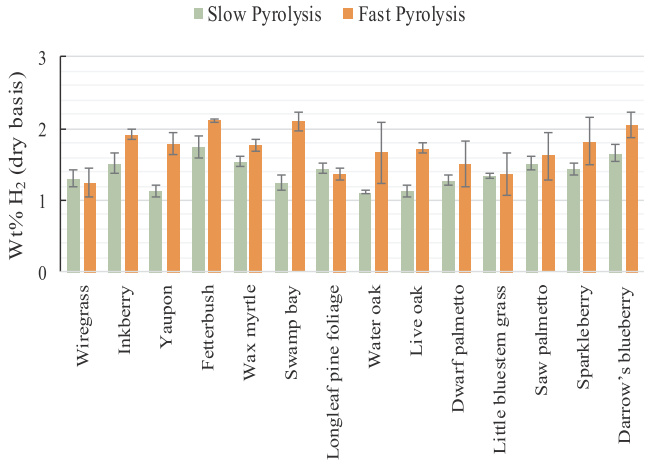

Fig. 10. The yield of H_2 wt% (dry basis) obtained from pyrolysis of live plant species.

However, at low pyrolysis temperatures, CO_2 forms due to the decomposition of cellulose and hemicellulose by the cracking and reforming of C=O and COOH functional groups. CO_2 may also form due to decarboxylation reaction [43]. By increasing the operating temperature, the CO_2 yield decreases, which seems to contribute to the increased formation of CO.

Little bluestem grass showed the highest CO_2 yield (42 wt%) for the slow pyrolysis experiments. For the fast pyrolysis experiments, swamp bay had the highest CO_2 yield (35 wt%). Little bluestem grass showed the largest difference in the CO_2 yield (13 wt%) between the slow and fast pyrolysis experiments.

Methane was the third most prevalent light gas observed in both the slow and fast pyrolysis of the plants. The yields of CH_4 were very similar for the slow and fast pyrolysis experiments. CH_4 is thought to form mainly due to the splitting of C-O bonds during lignin decomposition. In addition, CH_4 may also form due to removal of methoxy groups from the aromatic rings [44]. Dwarf palmetto (12 wt%) and Darrow's blueberry (11 wt%) showed the highest yields of CH_4 for the slow and fast pyrolysis experiments, respectively. In contrast with the yields of CO and CO_2, CH_4 did not show a consistent trend among the plant species when comparing slow and fast pyrolysis experiments. For example, yaupon showed a higher yield of CH_4 during fast pyrolysis experiments, while fetterbush had a higher yield of CH_4 during the slow pyrolysis experiments. The largest difference in the CH_4 yield (5 wt%) between slow and fast pyrolysis experiments was observed during the pyrolysis of dwarf palmetto.

H_2 yields varied between 1 and 2 wt% for both the slow and fast pyrolysis experiments. In most of the cases, slightly higher wt% of H_2 was formed in the fast pyrolysis experiments compared to the slow pyrolysis experiments. Two main mechanisms lead to the formation of H_2 at high pyrolysis temperatures. The first mechanism is the formation of H_2 from breaking of hydrogen bonds attached to the benzoic rings, which are present in the form of the phenolic groups in lignin structure [45]. The second mechanism is the decomposition of heavy gaseous hydrocarbons due to the secondary pyrolysis reactions, which leads to the formation of H_2 [41,44,46]. Darrow's blueberry showed the highest H_2 yields for both slow and fast pyrolysis experiments (1.7 and 2.1 wt%, respectively). The largest difference in H_2 yield between the slow and fast pyrolysis experiments was observed during the pyrolysis of swamp bay (0.9 wt%).

The results of analysis of light gas species for these experiments are summarized in Table 4. These results indicate that higher wt% of CO and H_2 were obtained in the fast pyrolysis experiments. In contrast, higher weight fractions of CO_2 were observed in the slow pyrolysis experiments. The CH_4 yield did not show a consistent trend among the plants when comparing slow and fast pyrolysis experiment. The average wt% of CO from the fast pyrolysis of all plant species was 57 wt%. However, the average CO yield was 49 wt% for the slow pyrolysis experiments. In contrast with CO, CO_2 showed a different trend; the average wt% of CO_2 from all slow pyrolysis experiments was 38 wt%, while this value was 29 wt% for the fast pyrolysis experiments.

3.3. Tar analysis

Tar is composed of complex mixtures of aliphatic and 1- to 5-ring aromatic compounds which are condensable at atmospheric temperature [47,48], although in this case condensable in the ice bath. At the end of the slow and fast pyrolysis experiments, the brownish tar compounds were extracted by dichloromethane as a solvent and then were analyzed using GC–MS. The tar species data for both slow and fast pyrolysis experiments were presented in previous publications [31,32]. Figs. 11 and 12 illustrate typical GC–MS chromatograms of tar for the same plant species (live longleaf pine foliage), which were obtained from the slow and fast pyrolysis experiments, respectively. While there is significant variation in tar species between plant species, these figures illustrate the general difference between slow and fast heating.

The chromatograms of the slow pyrolysis experiments illustrate that the majority of the identified tar compounds were C_5-C_{20} aliphatic and 1-ring aromatic compounds. The aromatic compounds had multiple attachments to the rings [32], such as a hydroxyl or ether group, with a smaller portion of alkyl or olefinic groups. Xu et al. [49] reported the

Table 4
Comparison of light gas compositions.[a]

	H_2 (wt%)		CO (wt%)		CO_2 (wt%)		CH_4 (wt%)	
Heating Rate	Average	Range	Average	Range	Average	Range	Average	Range
0.5 °C s^{-1}	1.3	1.1–1.7	48.6	47–58	35.9	34–42	7.5	5–11
180 °C s^{-1}	1.7	1.3–2.1	59.8	53–63	29.5	25–35	8.9	6–11

[a] wt% on a dry light gas basis.

presence of similar compounds during slow pyrolysis of red oak. The chromatograms of the fast pyrolysis experiments showed two 1-ring phenolic compounds with quite a few compounds with multiple aromatic rings. These multi-ring aromatic compounds had very few hydroxyl (OH) or other attachments on their rings [31].

Figs. 13 and 14 provide a typical comparison of the composition of tar compounds for the slow and fast pyrolysis experiment of longleaf pine. Results from the live foliage, dead foliage, and longleaf pine litter (dead and aged) are shown. The tar compounds with less than 0.1 mol% are not shown. Mole fractions of identified tar compounds were obtained by dividing their relative peak area to the total area of the peaks.

As shown in Fig. 13, primary tar compounds from the slow pyrolysis experiments were oxygenated 1-ring aromatic compounds, such as phenol, 1,2-benzendiol, 2-methoxy phenol, and 4-methyl phenol. The absence of multi-ring aromatic compounds and the presence of many alkyl and hydroxyl attachments seem to indicate that during these slow pyrolysis experiments, primary pyrolysis products did not undergo secondary pyrolysis reactions.

As shown in Fig. 14, phenol was still a major constituent of the tar from the fast pyrolysis experiment. However, other major tar compounds observed from the fast pyrolysis experiments were multi-ring aromatic compounds, such as naphthalene, fluorene, anthracene, phenanthrene, fluoranthene, and pyrene. The presence of multi-ring compounds seems to indicate that the primary pyrolysis products underwent secondary reactions and formed heavier polycyclic aromatic hydrocarbons (PAHs) in the fast pyrolysis experiments. The 1- and 2-ring tar species from the fast pyrolysis experiments still had some alkyl and hydroxyl groups, but not to the extent seen in the tars from the slow heating experiments. The aromatic compounds with 3 or more rings seen in the high heating rate experiments generally did not have attachments.

For the fast pyrolysis tars, the main constituents were generally phenolic compounds, such as 4-methyl phenol, 2-methoxy phenol (guaiacol), and 3,4-dimethyl phenol, which are mainly thought to evolve during pyrolysis of the plants due to the depolymerization of lignin building blocks [39,44,50,51]. Low molecular weight 1-ring aromatic compounds, such as benzene and phenol are thought to form during the decomposition of lignin [51,52]. Larger molecules, such as naphthalene, may be formed from 1-ring aromatic compounds by hydrogen abstraction and acetylene at high temperatures and heating rates (fast pyrolysis). Multiple-ring aromatic compounds may form from naphthalene via more complex mechanisms. For instance, by the addition of acetylene to naphthalene, acenaphthylene can form [53–55]. In addition, by increasing the pyrolysis temperature and heating rate, ketone, alcohol, and aldehyde content decreases due to the secondary reactions [41,54–57].

There were a few compounds, such as phenol, 1,2-benzenediol, and 4-methyl phenol, that were observed in both slow and fast pyrolysis tars. Figs. 15–17 show the mole% of these tar compounds during slow and fast pyrolysis of live plant species. The results indicate that for most of the plant species, the hydroxyl (OH) and methyl ($-CH_3$) attachments to the aromatic ring of phenols were removed during fast pyrolysis experiments, causing lower mole% of 1,2-benzenediol and 4-methyl phenol. The mole% of phenol in the tar generally increased for each plant species when the heating rate increased. Since the tar yield increased with heating rate, and the amount of multi-ring compounds increased in the fast pyrolysis tar, more phenol had to be formed in the fast pyrolysis experiment. The decrease in tar species such as 1,2-benzenediol and 4-methyl phenol coincide with the increase in phenol, indicating that some additional phenol was likely formed as alkyl and

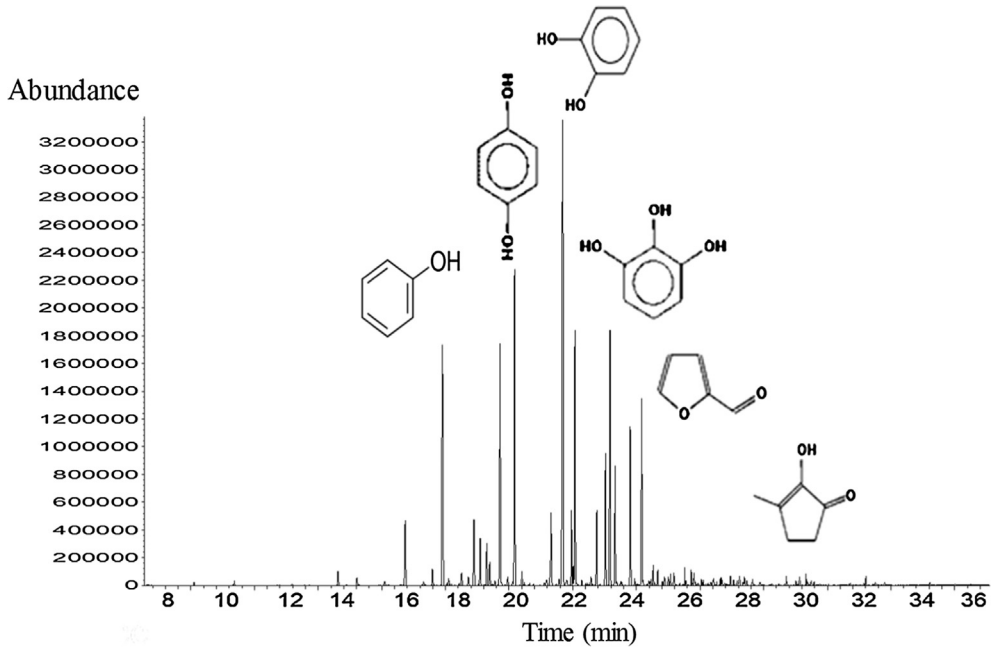

Fig. 11. GC–MS chromatogram of tar from the slow pyrolysis of live longleaf pine foliage.

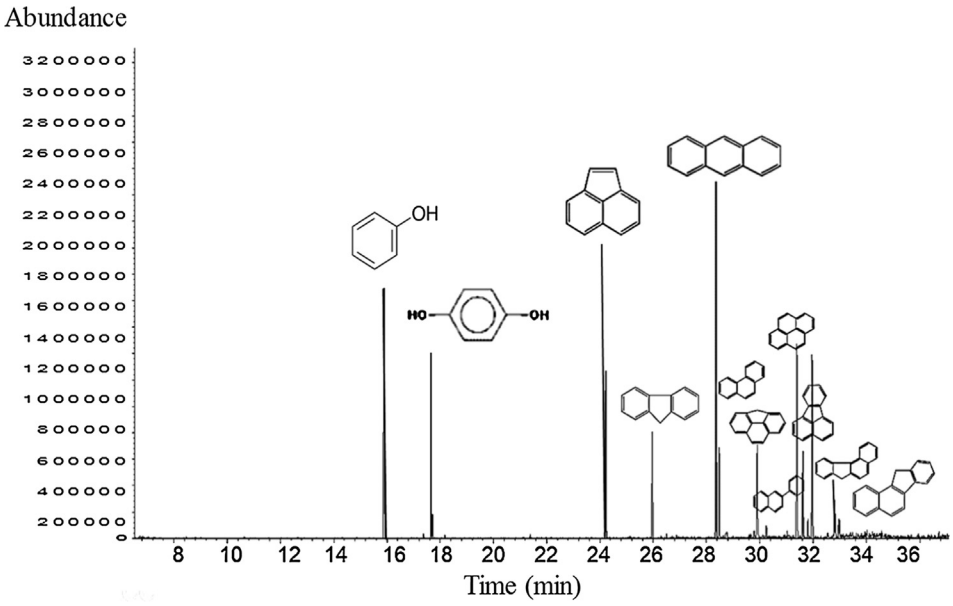

Fig. 12. GC–MS chromatogram of tar from the fast pyrolysis of live longleaf pine foliage.

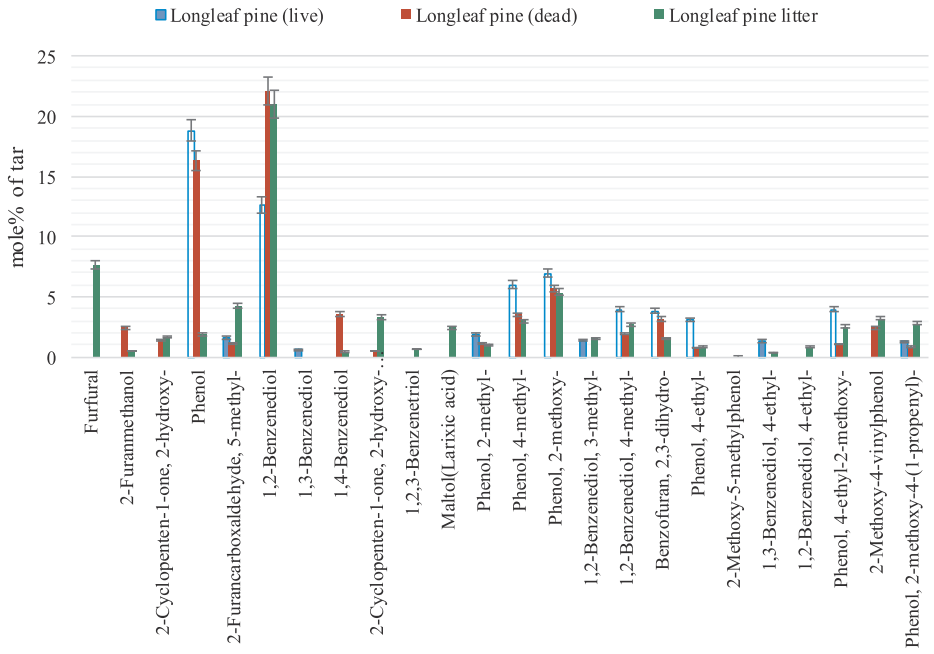

Fig. 13. Distribution of tar compounds for the slow pyrolysis of longleaf pine. Taken from [32].

hydroxyl groups are lost from 1-ring compounds. Radical sites formed on aromatic rings when alkyl and hydroxyl moieties are released may also be part of the mechanism for formation of multi-ring compounds through polymerization reactions.

4. Conclusion

In this study, the effects of pyrolysis temperature and heating rate on the yields and the compositions of pyrolysis products from 14 live plant species native to the southern forests of the United States were investigated. The main conclusions from this research are as follows:

1. The total volatiles yields were higher in the high heating rate experiments than in the slow heating rate experiments. The average volatile yield observed for all plants (live and dead) was 69 wt% (daf basis) at the slow heating rate but 80 wt% (daf) for the high heating rate.
2. Higher tar yields were obtained from the fast pyrolysis experiments. The average tar yield was 58 wt% (daf) for the fast pyrolysis experiments compared to 49 wt% (daf) for the slow pyrolysis experiments, an increase of 9 wt%. The average gas yields for the slow and fast pyrolysis of the plants were 20 and 22 wt%, respectively, which indicates the difference may be statistically insignificant.
3. By keeping the heating rate constant at 0.5 °C s^{-1} and increasing the pyrolysis temperature from 500 °C to 765 °C, char yield from longleaf pine litter only decreased from 27 to 25 wt%, indicating a 2 wt% increase in the volatile yield. In addition, tar yield decreased by only 2 wt% at the higher temperature (with low heating rate) due to the secondary reactions of tar compounds to increase the light gas yield.
4. By keeping the pyrolysis temperature constant at 765 °C, and increasing the heating rate from 0.5 °C s^{-1} to 180 °C s^{-1}, char yield from longleaf pine litter decreased noticeably from 25 wt% to 17%,

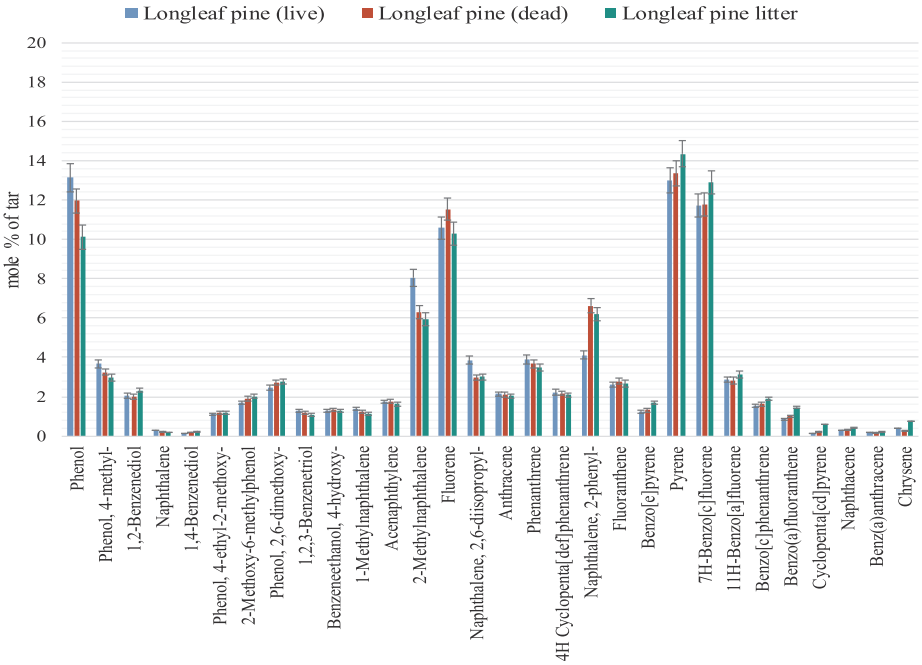

Fig. 14. Distribution of tar compounds for the fast pyrolysis of longleaf pine. Taken from [31].

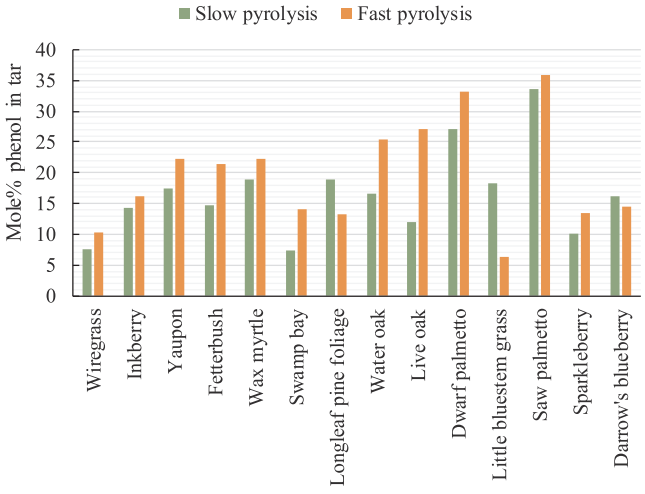

Fig. 15. Mol% of phenol in tar during pyrolysis of live plant species.

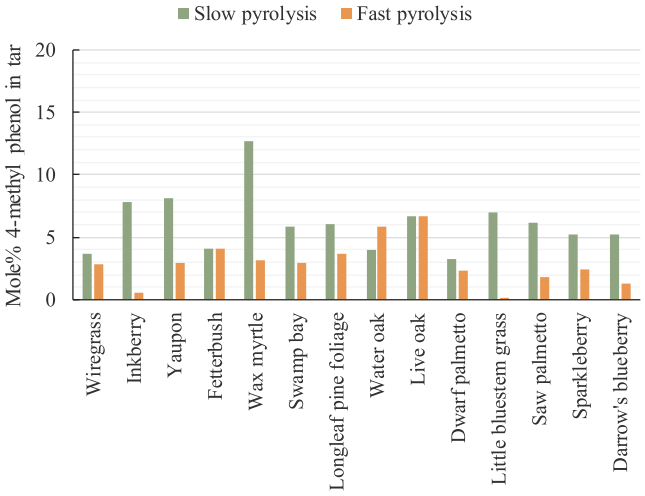

Fig. 17. Mol% of 4-methyl phenol in tar during pyrolysis of live plant species.

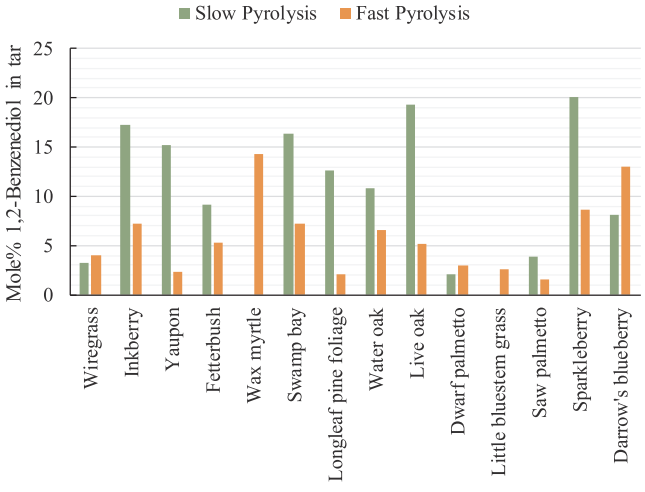

Fig. 16. Mol% of 1,2-benzenediol in tar during pyrolysis of live plant species.

which led to 11 wt% higher tar yield and 8 wt% higher total volatile yield. The increase in heating rate therefore seemed to have more effect on tar and total volatiles yield than final temperature for these experiments.

5. The major light gas species observed (on a wt% of dry gas basis) was CO, followed by CO_2, CH_4, and H_2, for both the slow and the fast pyrolysis experiments. Higher yields of CO were observed for all plants in the higher heating rate experiments. In contrast, higher yields of CO_2 were observed for slow pyrolysis of the plants compared to fast pyrolysis. The yields of H_2 were all small on a basis of wt% of dry light gas. The CH_4 yields did not show the same trend with heating rate for all plant species; some plants showed higher CH_4 yields in the fast pyrolysis experiment, while other plants showed higher CH_4 yields in the slow pyrolysis experiment.
6. There was a significant difference in the distribution of tar compounds during the slow and fast pyrolysis of the plants. Primary tar compounds from the slow heating experiments were some aliphatic hydrocarbons in addition to 1-ring aromatics with a large number of hydroxyl and alkyl attachments. In contrast, tar compounds from

the fast pyrolysis of the plants included phenol and a few other 1-ring compounds, but also included a significant amount of 3- to 5-ring aromatic compounds with very few attachments on the rings. Formation of heavy polycyclic aromatic hydrocarbons (PAHs) during fast pyrolysis experiments seems to indicate that primary tar compounds underwent secondary reactions in the gas phase.

7. Examination of common tar species observed in the slow and fast pyrolysis experiments showed that at least some of the phenol was created in the fast pyrolysis experiments due to the loss of hydroxyl and alkyl groups from other 1-ring species. Loss of hydroxyl and alkyl groups may also have formed radical sites on aromatic rings that contributed to polymerization that formed multi-ring compounds.

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