Production of Bio-Energy Feed stocks from Forest Understory Vegetation

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***Abstract*— The volume of biomass available in the understory of intensively managed pine stands remains unquantified. This study was designed to quantify this volume by stand type and to produce and determine the quality of a product from the harvested biomass. 1st thin, 2nd thin and clearcut stand types had 5 random plots assigned to each and understory biomass was harvested just prior to timber harvest. The forest lands on which the study was performed were managed by an industrial landowner. The forestlands were managed using intensive management practices including periodic control burns and fertilization. Biomass was harvested from the loblolly pine understory of each stand type just prior to a 1st or 2nd thinning and a final clearcut. Volume yield of understory biomass by stand type was computed. Elemental analysis was performed to characterize the biomass by stand type.**

Bio-oil was produced from the pyrolysis of the understory biomass harvested from each stand typeandbio-oil product yield was determined. Chemical and physical tests and higher heating value tests were performed to compare the bio-oil quality by stand type. The bio-oils produced from understory biomasses doesn't have the same quality compared to loblolly pinewood.

***Index Terms*— Understory, pyrolysis, bio-oil, pinewood, biomass.**

I. INTRODUCTION

The U.S. Billion-ton Update study published by DOE (2011)[1] indicates that the total of forest resources currently used was 129 million dry tons in 2011. Unused forest biomass comprised 97 million tons. Residues are an important component of this volume harvest that is really utilized for energy production. A component of harvest residues not adequately quantified and characterized to date is understory biomass in terms of volume, characteristics and potential for production of biofuels. Several studies have been performed that have determined the understory harvest volumes for integrated harvesting of southern pine stands [2, 3, 4, 5,6 and 7]. These studies harvested the round wood timber component, either simultaneously with, or just prior to, harvest of the understory component. Each study included small diameter unmerchantable stems, tops and limbs in the understory component. Such inclusion of non-understory harvest biomass sources masked the actual volume and characteristics of the true understory component.

This study was to determine the volume and quality of the understory component alone. The understory component was characterized physically and chemically. To determine the suitability of the understory alone as a biomass source capable of producing a product, the biomass was pyrolyzed to bio-oil and the bio-oil quality was analyzed.

This study was conducted on an intensively managed forest in which controlled burns or herbicidal applications were applied to the understory when it grew large enough in volume to compete with the resident timber.

It is very likely that intensively-managed stands may contain considerably less understory material than less well-managed stands. As an example, the understory component of the clearcut stand selected for this study became too vigorous during the rotation and was subjected to both a controlled burn and herbicidal release. In a less intensively-managed stand the heavily stocked understory would have been left intact until final harvest and considerably more volume would have been harvested than was the case for the current study. In the previous integrated studies cited above the understory biomass was only harvested at time of final clearcut. No measure of the volume available at intermediate thinnings has been made. It is possible, should the volume and quality of the understory biomass be sufficient, that understory harvest of the biomass during these intermediate thinnings would be feasible.

A study of the effect on soil chemistry of repeated slash removal in thinned stands has indicated only marginal and variable influence on long-term soil fertility [8]. Based on this result we hypothesize that the removal of understory vegetation will have a negligible influence on soil fertility. This is particularly true if the guidelines proposed in the Perlack[1] study are followed and 15% of the available biomass is left on the harvest or understory removal site.

It has been proven in slash bundler studies in post-harvest pine plantations that bundled harvest residue is suitable for bio-oil production with only a slight increase in ash content [9]. A recent study has also shown that young pines of 4 years of age produce bio-oil with acceptable quality. However, bio-oil produced from young 4-year old cottonwood saplings showed rapid viscosity increase, assumed to result from inclusion of bark and especially leaves in the feedstock [10]. Influence on bio-oil quality of inclusion of leaves in understory vegetation feedstock is unknown. However, it is well known that addition of 10 percent of methanol to bio-oil immediately after pyrolytic production will act to stabilize viscosity. Pine plantation understory biomass may, therefore, be available in both sufficient volume and quality to produce a bio-oil via pyrolysis, thus allowing a quality biofuel to be produced.

Raw bio-oils

Bio-oil is produced by flash pyrolysis of small biomass particles at 400 to 650^oC in the absence of oxygen. The yield of bio-oil is relatively high at 65 to75 percent dry weight basis or higher depending on the production process. Bio-oil chemical properties vary with feedstock type and applied pyrolysis conditions but woody biomass typically produces a mixture of 30-percent water, 30-percent phenolics, 20-percent aldehydes and ketones, 15-percent alcohols and 10-percent miscellaneous compounds [11].

As a fuel raw bio-oil has environmental advantages when compared to fossil fuels because combusted bio-oil produces lower to equal the NO_X, negligible quantities of SO_X and is CO_2 neutral. Raw bio-oils demonstrate some negative properties such as significant water content, high acidity, immiscibility with petroleum products, viscosity increase over time and a distinctive odor that have prevented its commercial use to date for other than pilot and demonstration projects. Bio-oil can contain up to 45-percent oxygen which is largely responsible for the various negative properties described. Researchers have concluded that raw bio-oils must be upgraded to use as a fuel for any purpose other than as a low-energy boiler fuel. Successful conversion of the raw bio-oil intermediate to above fuel depends on production of a high quality bio-oil.

II. MATERIALS AND METHODS

Understory biomass selection

Three stand types (1st thin, 2nd thin, and clearcut) were randomly selected from local loblolly pine industrial forest land in Alabama. Each stand type was bordered at least on one edge by a road or power line, providing a reference line to locate specimen plots. The reference line was divided into 100 ft. sections along the length of each stand. Five randomly generated sections were chosen from the total number of 100-ft. sections for each stand type. A 10’x10’ subplot was demarcated 100 ft. inside the stand from the reference line to ensure that the understory was not affected by abnormal exposure to sunlight.

All the green understory inside each 10’x10’ subplot was harvested and immediately processed with a wood chipper. The chipped understory material was placed into two 5-gallon containers and reweighed to determine the green weight. Samples of understory material were selected and ovendried to estimate the initial moisture content (MC) of the 10’x10’ subplot sections. The understory material from each subplot was dried in a Despatch Biomass Oven to below 10%MC and weights were recorded. A clear pinewood bio-oil was also prepared as a control biomass sample of known quality. Bio-oil from clear pinewood produced by the method applied in this study is known to be of high quality. The oven-dry weights from each of the 5 samples from each stand typewere prepared for pyrolysis by exactly the samesteps.The total biomass from each stand type was ground by a Bauer Grinder and screened to 1 to 3 mm particle size. Bio-oil was produced from the fast pyrolysis of the various feedstock types in an auger reactor.

Comparative stand management

The management of the three forest stand types was typical of industrial loblolly pine plantation management techniques. As indicated in **Table 1** the stands were very close in site index at 61, 60 and 65 for 1st, 2nd and clearcut stands, respectively. 1st thin, 2nd thin and clearcut stands were established , respectively, in 1996, 1988 and 1980 and had respective basal areas at harvest of 143, 100 and 98 indicating reduced stocking over time due to the thinning regime applied. As shown in **Table 2** the management treatments for each stand differed slightly depending on the status of each stand over time with management techniques applied in order to optimize timber volume yield. All stands were established by herbicidal chemical treatment after clearcut harvesting followed by burning of the residual stand. A controlled burn was performed on the clearcut stand in January of 2005 while the other stands were not subjected to controlled burns. Likewise, a mid-rotation herbicidal release was applied to the clearcut stand in August of 2004. Both the controlled burn and herbicidal release were performed to remove understory material competing with timber growth. All stands were fertilized during their growth with each stand receiving a diammonium phosphate (DAP) treatment realtively soon after establishment. Each stand was fertilized with urea approximately one year after the DAP treatment. The 2nd thin stand received an additional urea treatment 3 years after the second urea treatment while the 1st thin and clearcut stands received no additional fertilization after the first urea treatment.

Table 3 describes the sawtimber, chipping headrig and pulpwood stocking for each of the stands at the time of the 2008 sampling of understory biomass. The 1st thin was much more heavily stocked with smalldiameter timber such that it contained zero sawtimber and 63% less pulpwood than for the 2nd thin. The high basal area of 140 $ft^2$and the tonnage per acre of 788 indicates that considerable small diameter timber which did not make the sawtimber or pulpwood categories, was present on the stand. Therefore, as expected, the 1st thin stand was heavily stocked with small diameter timber with the expected shading of the site that would result from this fact. High shading should result in reduced understory volume as will be shown to be the case in data provided below. The 2nd thin stand had a modest volume of sawtimber, chipping headrig material and relatively high pulpwood volume. Considerably more light should have been available to reach the understory for a basal area of 100 ft^2compared to that of the 143$ft^2$1st thin condition comprised of the basal areas of small-diameter timber. Finally, the clearcut stand had a basal area nearly identical to that of the 2nd thin at 98 ft^2compared to 100 ft^2.However, this equivalent basal area was spread over a highly reduced number of stems such that crown interference with sunlight reaching the forest floor would have less interference from crown shading. However, it was the clearcut stand that was both control burned and subjected to a herbicidal release. Both these treatments would have served to dramatically reduce the understory volume on the final clearcut stand.

The influence of fertilization on the understory component was difficult to determine. Fertilization will result in increased understory growth but overtime the stand timber will grow faster to close the stand, thereby decreasing light penetration to the understory. It was not possible to determine the influence of fertilization on understory biomass yields during this study.

Table 1
Forest type, site index, age and basal area at harvest.

Stand Type	Forest Type	Site Index	Stand Establishment Date	Basal Area at Harvest (ft^2)
1st Thin	Loblolly Plantation	65	1996	143
2nd Thin	Loblolly Plantation	61	1988	100
Clearcut	Loblolly Plantation	60	1980	98

Biomass pyrolysis

A 3 kg/hr auger reactor constructed at the Department of Forest Products, Mississippi State University produced the bio-oil from the understory feedstock. The feedstock was pyrolyzed in the heated reactor tube as described earlier by Mohan *et al*. [12]. The pyrolysis temperature was set to approximately 450 ^oC and the vapor produced during this process exited the hot reactor zone and entered into the condenser train system. The temperature of the vapor decreased to approximately 100-110 ^oC by the end of the first condenser and in the second condenser it decreased to 30-50^oC. Thus, the bio-oil was collected from the condensers, and the non-condensable gases produced were collected in gas bags and analyzed using gas chromatography. Nitrogen gas was input to the reactor at a rate of 0.75 cubic feet/min. to assist in reducing air infiltration into the reactor.

Table 2
Silvicultural stand histories by stand type showing site prep, any controlled burns, herbicidal treatments and fertilization schedule.

Stand type	Site Prep	Controlled Burn	Mid Rotation Herbicidal Release	Fertilization		
				DAP[1]	Urea	Urea
1st thin	Chemical and burn 1998	None		Oct-06	Mar-07	None
2nd thin	Chemical and burn 1989	None		Aug-02	Jan-03	Mar-06
Clearcut	Chemical and burn 1982	Jan-05	Aug-04	Dec-02	Nov-03	None

[1]DAP is diammonium phosphate, a high phosphorous fertilizer.

Table 3
Per-acre stocking information for each of the three stand types.

Stand Type	Stand Age at Harvest (years)	Tons/ac at harvest	Sawtimber (MBF/ac)	Pulpwood (cords/ac)	Chipping HR (MBF/ac)[1]
1st thin	12	788	0	24.6	0
2nd thin	20	182	0	39.1	12.3
Clearcut	28	187	31.2	4.1	47.1

[1] Chipping HR (headrig) stems are too small to be processed as sawtimber on the main sawmill headrig. They are processed on a smaller high-speed headrig in the sawmill. Such stems are priced above the price of pulpwood but below the value of mature sawtimber.

Gas chromatography mass spectrometry analysis

A Hewlett Packard 5890 series II Gas chromatograph/5971 series mass spectrometer was used to analyze all bio-oil samples. A 30 m x 0.32 mm internal diameter x 0.25 μ silica capillary column coated with 5% phenylmethylpolysiloxane was used as GC column. The temperature was increased from 40 °C (4 min hold) to 280 °C at a heating rate of 5 °C/min. The mass spectrometer employed a 70 eV electron impact ionization mode, a source temperature of 250 °C and an interface temperature of 270 °C.

A 0.1 mg bio-oil sample was diluted in 10 ml of methanol. One ml of this representative solution was then transferred to the autosampler vial and mixed with 10 µL of internal standard. Then 2.0 µL of this sample was injected to the GC column to obtain the chromatogram. Six isotopically labeled compounds (US 108N, Ultra Scientific: 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenapthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}) were used as the internal standards.

Gas analysis

Gas samples from each pyrolysis treatment were analyzed on a Varian CP-4900 Micro Gas Chromatograph which contained 4 individual GC channels. A ten meter MS5A GC column was used in channel no. 1 and 10 meters PPQ GC column was used in channel no. 2. Channel no. 1 was utilized to analyze hydrogen, oxygen, nitrogen, methane, and carbon monoxide concentrations and channel no. 2 analyzed the concentrations of carbon dioxide and ethane. For channel no. 1 injector temperature and the column temperature were 50 and 80°C, respectively. For channel no. 2 the injector temperature was 110 °C and column temperature was 60°C. A mass balance of the product yield was performed based on these results.

Gel permeation chromatography

Gel permeation chromatography (GPC) analyses of all samples were performed to determine number averaged molecular weight (M_n), weight averaged molecular weight (M_w) and the polydispersity index.

Physical analysis

The water content, pH, density, acid value and viscosity of each bio-oil were determined by using the appropriate ASTM standard. Percent water was measured by Karl Fisher titration with a Cole-Parmer Model C-25800-10 titration apparatus (ASTM E203). pH was determined with an expanded ion analyzer EA 920. Viscosity was measured using a Rheotek viscometer at 40°C temperature (ASTM D7544). Acid value (ASTM D664) was calculated by dissolving 1 g of the bio-oil to 50/50 (v/v) isopropanol/water mixture and titrated with 0.1N NaOH to a pH of 8.5. Density was determined based on ASTM D4052.Flash point values of all bio-oil samples were determined via a flash point analyzer from Koehler Instrument Company, Inc. in accordance with ASTM standard D7215-08.Elemental analyses of all biomass and bio-oils were performed by an Exeter CE-440 elemental analyzer. Higher heating values (HHV) of the same samples were measured by a Parr 6200 calorimeter. Lignin content of the three biomass samples was performed following TAPPI 22 method by Galbraith Laboratories, Knoxville, Tennessee.

Principal component analysis

Principal Component Analysis (PCA) of the GC/MS spectral data was performed to identify qualitative differences in the bio-oils based on the feedstock types. The multivariate data analysis was performed with Unscrambler version 9.7 (CAMO, Corvallis, OR, USA). PCA was performed using five repetitions from GC/MS analysis spectral data. The total ion current from each individual scan of the mass range 35 to 550 Daltons was usual for the PCA analysis. Each chromatogram contained approximately 6000 scans. The spectral chromatographic data was used as data and the 4 different bio-oils from different feedstocks were used as samples in the PCA. The score plots explain the peaks which are largely responsible for any differentiation of the bio-oil types.

III. RESULTS AND DISCUSSION

Table 4 shows the stand age and the total amount of understory biomass collected from the five 10’x10’ sections of 1st thin, 2nd thin and clearcut loblolly pine stand types. For each stand type, a total area of 500 sq. ft. of understory was collected and oven dried. Since there are 43,650 sq. ft./acre, the total oven dried ton/acre (dt/a) was calculated to be 3.36 dt/a for clearcut, 7.85 dt/a for 2nd thin, and 3.49 dt/a for 1st thin loblolly pine stand types. These yields indicate that both the

1st thin and clearcut stand had increased shading compared to the 2nd thin with the result that less biomass was able to grow under the stand crown.

Pyrolysis product yields

Table 5 summarizes the bio-oil, char and gas yields from the pyrolysis of the three biomass samples: 1st thin, 2nd thin and clearcut loblolly pine. These values are compared to data from bio-oil produced from clear pine wood subjected to the same preparation and pyrolysis conditions as the stand type biomass samples. A mass balance was performed based on the gas analyses results of the non-condensable gases. The results showed that the clearcut biomass produced 50 wt% bio-oil, 24 wt% char and 8.83 wt% of non-condensable gases. 1st thin and 2nd thin produced 38 and 45 wt% bio-oil, 33 and 26 wt% char and 5.11 and 13.84 wt% of non-condensable gases, respectively.Clear pinewood produced 60.0 wt% of bio-oil, 22% of char and 7.6 wt% of non-condensable gases. As is typical of pyrolysis studies the mass balance did not close to 100%.

Table 4

Stand age and amount of understory from five 10'x10' sections by stand type.

Stand type	Stand age (years)	Green collected understory (lb)	Green MC (%)	Oven dried collected understory (lb)	Oven dried ton/acre
1st thin	12	158.7	101.2	80.0	3.5
2nd thin	20	327.4	84.0	180.2	7.9
Clearcut	28	165.3	121.8	77.1	3.4

Table 5

Bio-oil, char and gas yields produced from the pyrolysis of harvested pine understory biomass by stand type.

Stand Type	Bio-oil (wt%)	Char (wt%)	Non-condensable gases (wt%)	Total (%)	Ash (wt%)	Water content (%)	HHV (MJ/Kg)
1st thin	38.0	33.0	5.1	76.1	2.77	51.85	17.7
2nd thin	45.0	26.0	13.8	84.8	2.54	36.74	18.6
Clearcut	50.0	24.0	8.8	82.8	2.73	42.19	18.8
Clear pinewood	60.0	22.0	7.6	89.6	0.50	20.83	18.6

The main reason for the lower bio-oil yields from the understory biomass is the ash content (ranging from 2.54 to 2.77%) of the understory biomass compared to that for clear pine wood (0.50). Both leaves and bark contained in the understory material will contain relatively high mineral content which will result in a high ash volume. The presence of minerals in pyrolyzed feedstock has been shown (13) to have a major influence on reducing bio-oil yield. This reduction is due to the catalytic effect of the minerals during pyrolysis that tend to increase the char and non-condensable gas volumes produced. The 1st thin yield of 38 wt% was just slightly over half of the 60% produced for clear pine wood. In this case the mineral content appears to have catalyzed very high char production (33.0 wt%) compared to 22.0 wt% for clear pine wood. The high production of char volume was at the expense of both liquid bio-oil and non-condensable gases for the 1st thin feedstock type which produced 5.1 wt% of gas compared to the 7.6 wt% for clear pine.

The 2nd thin and clearcut bio-oil yields (45 and 50 wt%, respectively) were considerably higher than the 38.0 wt% obtained for the 1st thin although they are far short of the 60 wt% volume produced from clear pine wood. The 2nd thin and clearcut char volumes are also much closer to those for pine clear wood at 26.0 and 24.0 wt%, respectively. The fact of less char production for the 2nd thin and clearcut resulted in favoring more non-condensable gas production than for clear pine wood (7.6 wt%) at 13.8 and 8.8 wt% , respectively. It appears that, in spite of the similar ash value for the 1st thin when compared to the 2nd thin and clearcut, some factor present in the 1st thin biomass caused a high production of char at the expense of bio-oil yield.

In addition to reduction of bio-oil yield at the expense of char and gas production high mineral content (>1.2) has been shown[14]to also catalyze high water production during pyrolysis. In the case of the understory biomass types resulting in water content values were very high at 42.19, 51.85 and 36.74 wt% for 1st thin, 2nd thin and clearcut, respectively, compared to 20.83 wt% produced for clear pinewood.

Table 6 compares the pH, acid value, density, water content and the viscosity of the three understory bio-oils and that for clear pine wood. The high water content values produced by mineral catalysis during pyrolysis have already been discussed. However, the high water content values had a direct effect on the viscosity of the three understory bio-oils with values of 4.5, 3.0 and 5.8 for 1st thin, 2nd thin and clearcut, respectively, compared to 6.5 for the the clear pine bio-oil. This is due simply to the effect of bio-oil dilution by the water. While there were minor differences in acid value, density and pH between the bio-oils by stand type these were very minor and no conclusions can be drawn from them. However, it is clear that the understory bio-oils tend to have higher acidity than for clear pine wood. Again, catalysis during pyrolysis by minerals contained in the understory biomass types appear to catalyze increased production of carboxylic acids compared to the production for clear pine wood.

Table 6

Results of physical analysis comparison-of-means tests from bio-oils produced from pyrolysis of harvested pine understory biomass.

Sample name	pH	Acid value (mg KOH/g)	Density (g/cc)	water content (wt%)	Viscosity (cSt)
Clearcut	2.69	113.98	1.12	42.19	4.6
1st thin	2.76	92.84	1.11	51.85	3.0
2nd thin	2.67	107.61	1.11	36.74	5.8
Clear pinewood	2.65	90.06	1.17	20.83	6.5

The data in **Tables 5** and **6** indicate that some factor, other than ash content, influenced the quantity of bio-oil and other products produced from the 1st thin stand compared to the 2nd thin and clearcut stands. The difference caused by this unknown factor will be indicated by other results of the current study and indicates that the understory vegetation of the 1st thin stand differs in some way from the understory vegetation of the other two stand types.

Gel permeation chromatography (GPC)

The averaged molecular weights (M_w) for the three stand types were measured by gel permeation chromatography. M_w values were 548, 583 and 605, respectively, for the 1st thin, 2nd thin and clearcut treatments. The 1st thin value of 548 M_w was considerably lower than for the 2nd thin and clearcut treatments with their values of 583 and 605M_w, respectively. This indicates that the high production of water and char produced during pyrolysis of the 1st thin biomass appear to have both contributed to a lower molecular wt for the 1st thin bio-oil.

Elemental analysis and higher heating value

Table 7 gives the elemental C,H, N and O (by subtraction) measured in the biomas types and compared to the values for clear pinewood. This analysis shows that there is considerably less carbon in the understory biomass types (46.4, 47.2 and 47.0 wt%) than for clear pine wood (50.9%). This was the expected outcome because of the leaf content of the understory biomass types. Leaves contain considerably less lignin than clear wood and lower lignin translates to less carbon content. There is little difference in the hydrogen values by biomass type but nitrogen is much lower for clear pinewood (0.2 wt%) than for the understory biomass types (0.8, 0.5 and 0.8, repectively, for 1st thin, 2nd thin and clearcut). This is, again, an expected result as leaves will contain more nitrogen than clear wood. The oxygen values are all about the same for the understory biomass types (ranging between 46.5 to 47.1 wt%) but are higher than the 41.7% for clear pinewood. This was probably due to the fact that leaves apparently contain more bound oxygen than clear wood.

Table 7

Elemental analyses and higher heating values of harvested pine understory biomass by stand type.

Sample name	C (wt%)	H (wt%)	N (wt%)	R (wt%)	HHV (MJ/Kg)
1st thin	46.4	5.7	0.8	47.1	17.7
2nd thin	47.2	5.6	0.5	46.6	18.6
Clearcut	47.0	5.8	0.8	46.5	18.8
Clear pine wood	50.9	6.1	0.2	41.7	18.6

Table 8 gives the elemental C, H, N and O (by subtraction) and HHV of these three understory bio-oils along with values for clear pine wood for comparison. The carbon value for 1st thin was very low at 26.4 compared to 38.6, 35.5 and 36.2 for 1st thin, 2nd thin, clearcut and clear pine wood, respectively. The low carbon value for the 1st thin bio-oil is totally due to its high water content of 51.81 % compared to 42.1 and 36.74 % for clear cut and 2nd thin bio-oils, respectively. The high water content would dilute the carbon contained in the organic content. Again there is little difference in the hydrogen values by bio-oil type but the 1st thin bio-oil does contain more hydrogen and oxygen than those produced from other biomass types. This stems from the high water content of the 1st thin bio-oil. It is somewhat surprising that the hydrogen value is not higher given this fact. The oxygen value for the 1st thin bio-oil fits the fact of much higher water content in the 1st thin bio-oil (64.3 wt%) compared to the water content value for the bio-oils from the other biomass types (52.4, 55.4 and 55.9 wt%, respectively). The high water content and low carbon content of the 1st thin bio-oil explains why the 1st thin bio-oil did not burn to give a higher heating value. The lower HHV values for the 2nd thin and clear cut bio-oils are, again, explained by the high water content of these bio-oils compared to that for the clear pine wood.

Table 8

Elemental analyses from bio-oils produced from pyrolysis of harvested pine understory biomass by stand type. Oxygen was determined by the difference of the measured C,H and N and the total gas wt%.

Stand type	C (wt%)	H (wt%)	N (wt%)	R (wt%)	HHV (MJ/Kg)
1st thin	26.4	8.5	0.8	64.3	Didn't burn
2nd thin	38.6	7.9	1.1	52.4	15.19
Clearcut	35.5	8.1	1.0	55.4	15.01
Clear pine wood	36.2	7.8	0	55.9	16.3

Loblolly pine 1st thin biomass had a lower heating value (17.65 MJ/Kg) compared to those for the other biomasstypes and the bio-oil produced from this material did not burn at all. This is explained by the fact that this bio-oil had a much higher water content (51.85%) which prevented burning. The heating values of the bio-oils produced from clearcut and 2nd thin loblolly pine were 15.01 and 15.19 MJ/Kg, respectively, which were much less than their corresponding biomass samples (18.82 and 18.61 MJ/Kg, respectively).

Lignin, cellulose and hemicelluloses content analysis

Table 9 indicates the percentage of lignin, cellulose and hemicelluloses present in each of the three biomass samples. Clearcut loblolly pine had the significantly highest lignin percentage at 30.0 wt%. Significantly lowest lignin content was for the 2nd thin stand at 27.2 wt%. Lignin content of the 1st thin stand was slightly lower than for the clearcut stand which contained lignin of 29.3 wt%. It is likely that the 2nd thin stand lower lignin content resulted from the ability of released understory biomass to produce more herbaceous growth following its release by the 1stthin such that more sunlight was able to reach the understory. Cellulose content of the understory biomass types was substantially lower for all understory biomass types (ranging from 33.2 to 35.7 wt%) compared to clear pinewood at 39.5. Hemicelluloses is considerably higher for all understory biomass types (ranging from 20.9 to 24.5 wt %) compared to the 19.8% value measured for loblolly pine. However, the published value range for southern pine is 20.5 to 27.5 wt% of hemicelluloses [15]. The measured value for clear pinewood for the current study was slightly below this range but the measured values of hemicelluloses for the understory biomass types were within this range.

Table 9

Cellulose, hemicelluloses and lignin wt% values of understory and clear pinewood biomass based on Klason lignin results. To reduce expense only a single Klason lignin test was performed at Galbraith Laboratories to obtain these values.

	Stand type			
	1st Thin	2nd Thin	Clearcut	Clear pinewood
Cellulose (wt %)	33.2	35.7	34.1	39.5
Hemicellulose (wt %)	23.2	20.9	24.5	19.8
Lignin (wt %)	29.3	27.2	30.0	27.8

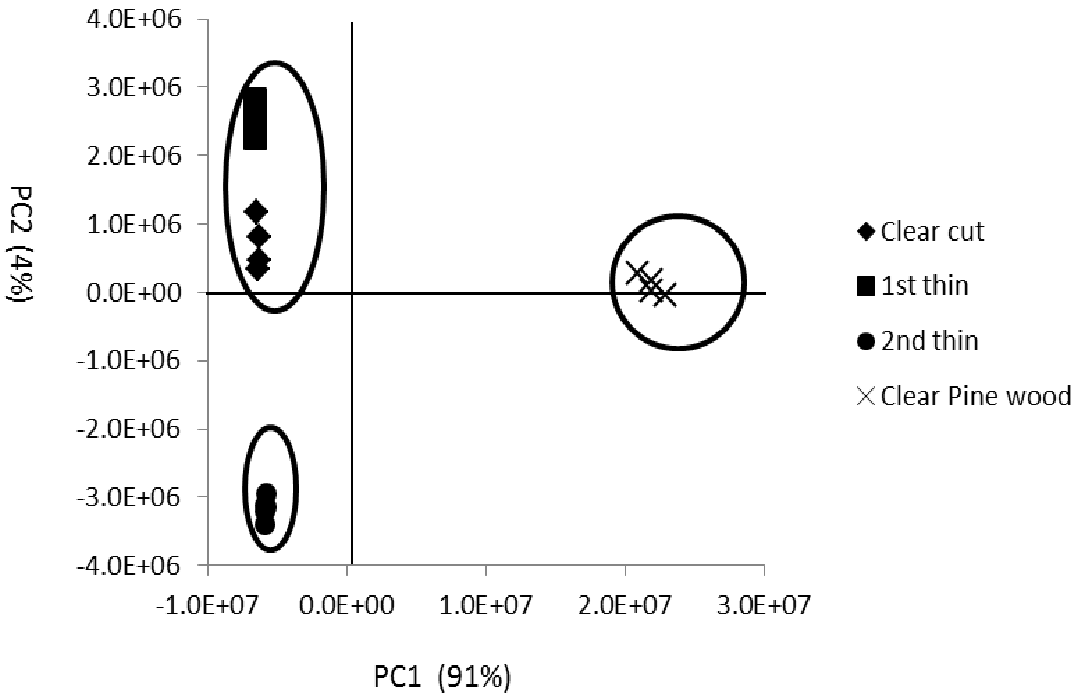

Figure 1.Princiapal component score plot showing bio-oil clustered with different understory biomass

Principal component score plot showing clear pinewood bio-oil clustered separately from other understory bio-oils along the PC1 axis indicating that this bio-oil had a different chemical composition than all other types. The clearcut and 1st thin stand clustered to the positive side of the PC2 axis indicating similar chemical spectra in the bio-oil of each. The 2nd thin stand clustered toward the negative side of the PC2 axis indicating that1st thin bio-oil differed from 2nd thin and clearcut understory bio-oils in chemical spectra. However, as the PC2 axis explains only 4% of total analysis variance the differentiation of the 2nd thin bio-oil is relatively weak.

Principal component analysis

The chromatograms (GC/MS) of all the four bio-oil types were compared by principal component analysis to distinguish them based on their chemical fingerprints. Figure 1 is a scores plot of PC1 and PC2 where PC1 explains 91% of the total variance. Three distinct clusters are observed in the score plot based on the biomass types from which bio-oils were produced. Bio-oil produced from different stand types clustered completely separately from the clear pine bio-oil along PC1 axis. The clear pine bio-oil difference is a strong one because the PC1 axis explains 91% of the variance. The bio-oils produced from clearcut and 1st thin stand types clustered together indicating similarities in their chemical properties. The 2nd thin type is separated from other stand types by the PC2 axis but this axis explains only 4% of the total variance of the analysis which is a small difference. This indicates that the 2nd thin bio-oil did not differ greatly from the 1st thin and clearcut understory bio-oils. However, the 2nd thin bio-oil did contain much less water (36.7 wt%) compared to the other two understory bio-oils which contained 51.9 in the 1st thin bio-oil and 42.2 in the clearcut bio-oil. This physical difference confirms the weak differentiation of the 2nd thin bio-oil based on principal component analysis.

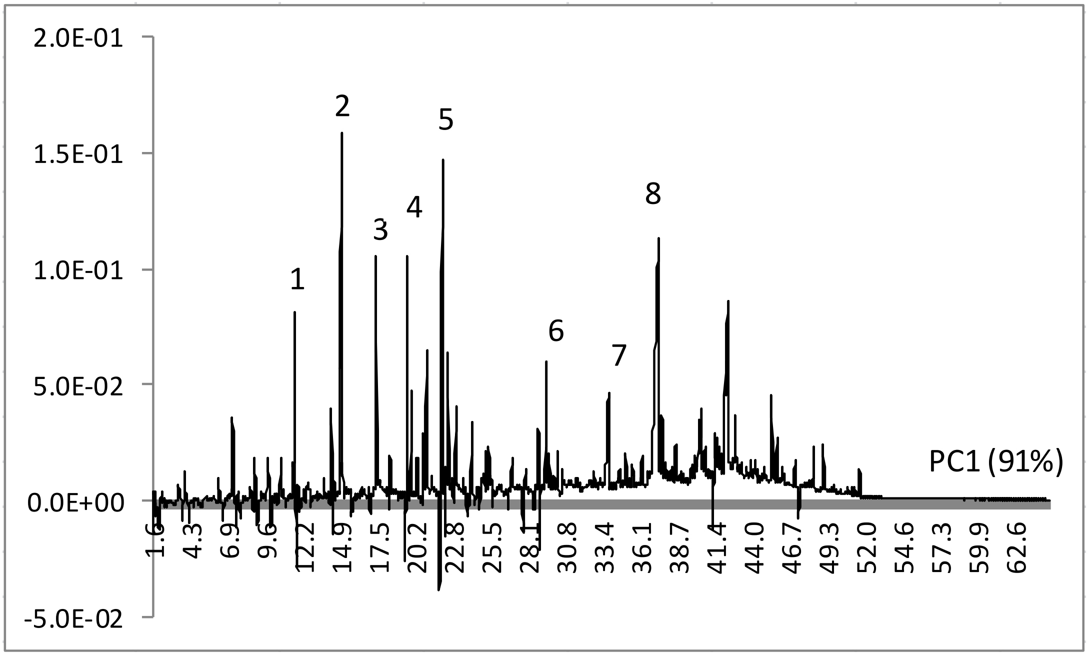

Figure 2.PC1 loadings plot indicating the important spectral peaks responsible for the classification of clear pinewood and the three understory bio-oil types.

The loadings plot along PC1 (**Figure 2**) indicates the important peaks responsible for the classification between clear pine wood bio-oil and other understory bio-oils. These were 4-methylphenol (1), 4-methylguaiacol (2), 4-ethylguaiacol (3), syringol (4), 4-methylsyringol (5), 3,5-dimethoxy-4-hydroxyphenylacetic acid (6), 3,4-dimethoxycinnamic acid (7) and levoglucosan (8). Interpretation of the positive sign of the loadings along PC1axis indicates that clear pine wood bio-oil contained a higher amount of lignin fractions (guaiacol and syringol units) and levoglucosan (polysaccharide) compared to the understory bio-oils. **Figure 3** shows the loadings plot along the PC2 axis indicating that the important peaks for separate clustering of the 2nd thin bio-oil from 1st thin and clearcut bio-oils were syringol (4), 4-methylsyringol (5) and phenol, 2,6-dimethoxy-4-(2-propenyl) (9). Interpretation of the negative loadings along PC2 indicate that 2nd thin type bio-oil has a higher amount of syringol lignin fractions compared to the 1st thin and clearcut bio-oils.

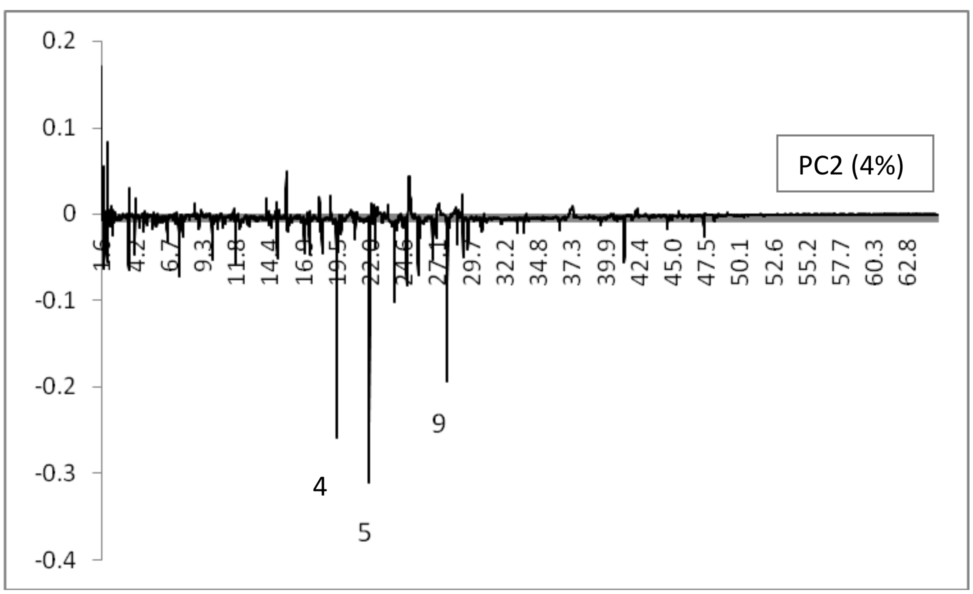

Figure 3.PC2 loadings plot indicating the important spectral peaks responsible for the classification of clear pinewood and the three understory bio-oil types.

IV. CONCLUSIONS

The understory components present just prior to harvesting 1st thin, 2nd thin and clearcut loblolly pine stands were collected from5 randomly sampled plots for each stand type located on an intensively managed industrial forest. Clear pinewood biomass and bio-oil were produced by biomass preparation and pyrolysis techniques in the same manner as were the understory bio-oils to provide a high quality biomass and bio-oil for comparative purposes. The three stand types were managed similarly with the exception that the clearcut stand required a controlled burning and a herbicidal treatment to reduce competition from understory vegetation with the pine stand. Chemical and physical tests were performed to analyze the properties of biomass and bio-oil produced from the stand type and the clear pinewood biomass.

Yields of understory biomass form the three stand types were 3.5, 7.9 and 3.4 dry tons per acre for 1st thin, 2nd thin and clearcut stand types. Pyrolysis of theclearcut biomass produced 50 wt% bio-oil, 24 wt% char and 8.83 wt% of non-condensable gases. 1st thin and 2nd thin produced 38 and 45 wt% bio-oil, 33 and 26 wt% char and 5.11 and 13.84 wt% of non-condensable gases, respectively.Clear pinewood produced 60.0 wt% of bio-oil, 22% of char and 7.6 wt% of non-condensable gases. This result of much lower bio-oil yields for the understory biomass compared to the clear pine was clearly due to the high mineral content of the understory biomass types as evidenced in their high ash values(2.77, 2.54, 2.73 for 1st thin, 2nd thin and clearcut, respectively). Clear pinewood had an ash value of only 0.50%. In addition to lower bio-oil yields at the expense of char and gas production the high mineral contents of the understory biomass resultedin production of very high bio-oil water content values of 42.19, 51.85 and 36.74 wt% for 1st thin, 2nd thin and clearcut, respectively, compared to 20.83 wt% produced for clear pinewood bio-oil. Acid value and density of the bio-oils produced from the understory biomass types did not differ greatly among themselves or in comparison to the clear pinewood bio-oil.

Elemental analysis results performed on the biomass types showed the carbon content of the understory biomass types to be about the same, ranging from 46.4 to 47.2 wt% compared to 50.9% for clear pinewood. In this case, based on the result reported in Table 9, it appears that the carbon reduction for the understory biomass types was probably due to the presence of a substantial leafy percentage contained in the understory biomass types.

The chromatograms (GC/MS) of all four bio-oil types were compared by principal component analysis. The PC1 score plot was found to explain 91% of total analysis variance. The bio-oil types grouped into three distinct clusters in the score plot. The clear pine bio-oil plotted as a cluster in a completely separate location in the score plot indicating high difference in spectral components compared to the understory bio-oils. The bio-oils from the clearcut and 1st thin stand biomass types clustered together indicating high similarity. The 2nd thin bio-oil type clustered on the same side of the PC2 axis but below the PC1 axis. This indicates a substantial difference between the bio-oil produced from the 2nd thin biomass compared to bio-oils from all other biomass types.

Principal component analysis showed that clear pine bio-oil was differed strongly in chemical composition from the three understory bio-oil types as the PC1 axis explained 91% of total analysis variance. But, the three understory bio-oils types were chemically very similar as the PC2 axis explained only 4% of total analysis variance. The 2nd thin bio-oil was separated from 1st thin and clearcut by the PC2 axis indicating a small difference in the chemical fingerprint. Physical analysis results of these bio-oils showed that 2nd thin type had much lower water than other two understory bio-oil types confirming the difference shown by principal component analysis.

The results of this study indicate that the yields of biomass available from understory biomass in intensively-managed stands are considerable but are likely not large enough to justify the expense of collecting them by a non-integrated method. In addition the bio-oil quality produced from these understory types provides both low yield and high water content which result from the high mineral content of the understory biomass compared to clear pine wood. This high mineral component acts as a catalyst to convert what would normally become liquid bio-oil into char, gas and water.

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