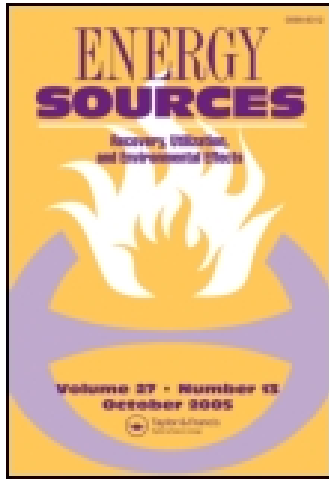


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## Energy Sources, Part A: Recovery, Utilization, and Environmental Effects

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/ueso20>

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Published online: 06 Mar 2015.

To cite this article: H. Ravindran, S. Thangalazhy-Gopakumar, S. Adhikari, O. Fasina, M. Tu, B. Via, E. Carter & S. Taylor (2015) Production of Bio-oil from Underutilized Forest Biomass Using an Auger Reactor, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 37:7, 750-757, DOI: [10.1080/15567036.2011.613894](https://doi.org/10.1080/15567036.2011.613894)

To link to this article: <http://dx.doi.org/10.1080/15567036.2011.613894>

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# Production of Bio-oil from Underutilized Forest Biomass Using an Auger Reactor

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Conversion of underutilized forest biomass to bio-oil could be a niche market for energy production. In this work, bio-oil was produced from underutilized forest biomass at selected temperatures between 425–500°C using an auger reactor. Physical properties of bio-oil, such as pH, density, heating value, ash, and water, were analyzed and compared with an ASTM standard to document the effect of pyrolysis temperature. All of the properties analyzed in this study, except for the ash content of the bio-oil, met the ASTM standard. Chemical composition of bio-oil was also analyzed, and the concentration of each species was compared at different temperatures.

*Keywords:* auger reactor, bio-char, bio-oil, fast pyrolysis, underutilized forest biomass

## 1. INTRODUCTION

Environmental concerns, national energy security, and climate change are the primary reasons to explore bio-based energy sources. Two major platforms for converting biomass to fuels are thermochemical and biochemical. Fast pyrolysis, a thermochemical process, has attracted a lot of interest because of its high liquid fuel (bio-oil) production and feedstock flexibility. The products of the fast pyrolysis process are bio-oil, bio-char (solid left after pyrolysis), and gases, in which bio-oil is the major product. Bio-oil is in the form of liquid that can be easily stored and transported, and this could reduce the issues related to biomass logistics.

In the fast pyrolysis process, biomass is heated rapidly under inert conditions to decompose it into vapors, aerosols, gases, and bio-char. These vapors and aerosols are rapidly quenched in a condenser to produce liquid known as bio-oil. This liquid has numerous compounds, such as water, acids, aldehydes, ketones, sugars, esters, phenols, cresols, furans, and guaiacols (Diebold, 2000). Bio-oil can be used for several applications, such as heat and power generation and fossil fuel

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replacement (Czernik and Bridgwater, 2004). In addition, it is also used in chemical industries to produce various useful products and in the food industry as a preservative.

Feedstock agnostic is a major advantage of a pyrolysis process compared to other thermo- and bio-chemical platforms. Different biomass types, such as bagasse, pinewood, hazel nut shell, pine sawdust, switchgrass, mixed wood waste (mixture obtained from different wood shaving), rubber (tire wastes), and plastic as feedstocks, have been used for the pyrolysis process. Based on the Billion-Ton study, the U.S. has a capacity to produce about 368 million dry tons of forest biomass annually (Perlack et al., 2005). Forest biomass includes logging residues, residues from forest thinning, fuel wood, primary and secondary wood processing mill residues, black liquor, and urban residues. A forest thinning operation helps to prevent forest fire hazards and improves forest productivity and forest health. Thinning operation will leave some residues, such as woodchips, barks, twigs, and dry leaves, which have no market value. This biomass currently has little or no value because there is no commercially proven method to process such diverse biomass. In addition, it is very difficult to manage this bulky and light biomass compared to other logging residues. The authors in this study have used this biomass as a feedstock for the pyrolysis process, and analyzed selected properties of the bio-oil obtained.

## 2. MATERIALS AND METHODS

### 2.1. Biomass Preparation and Characterization

In this study, underutilized forest biomass (UFB) used for the fast pyrolysis process was obtained from the USDA–Forest Service at Auburn, Alabama. The biomass consists of woodchips, barks, twigs, dry leaves, and other residues acquired from a forest thinning operation. Biomass was dried in an oven for 24 h at 75°C, mixed well, and ground using a hammer mill (New Holland grinder model 358) fitted with 3.175 mm (1/8 in.) screen size. The powdered sample was considered as the homogeneous mixture of these components, such as chips, barks, twigs, and leaves. The biomass sample was fractionated through a simple sieve analysis, and the particles in the range of 0.841 to 1.41 mm (U.S. Sieve No. 14–20) were considered for this study. Bulk density of the biomass sample was calculated by filling the biomass in a given volume of a graduated cylinder (100 mL) and measuring the weight of the cylinder with and without biomass. Moisture and ash contents of the biomass (wet basis) were determined according to the ASTM E 871 and ASTM E 1755 standards, respectively. An oxygen bomb calorimeter (IKA, model C200) was used to measure the higher heating value (HHV) of biomass. Chemical constituents of the biomass sample were analyzed in the Bioenergy Laboratory at the Center for Bioenergy and Bioproducts of Auburn University according to “Standard Biomass Analytical Methods” developed by the National Renewable Energy Laboratory.

### 2.2. Bio-oil Production Using Auger Reactor

Underutilized forest biomass was converted into bio-oil using an auger reactor, designed and fabricated at Auburn University (Thangalazhy-Gopakumar et al., 2010). The reactor was operated at four different temperatures (425, 450, 475, and 500°C) to investigate the effect of temperature on bio-oil yield and its physical properties. The temperature range for pyrolysis was selected after some preliminary studies in this reactor with different types of biomass. For each experiment, a known amount of biomass (500 g) was fed into the auger reactor to produce bio-oil, and the reactor was maintained at inert atmosphere by purging nitrogen gas before the pyrolysis process. The temperature in the reactor was heated to the desired temperature and held for 5 min to avoid the temperature gradient inside the reactor. The biomass from a hopper was then passed to the reactor

using a screw feeder. The temperature of the reactor was measured by two thermocouples attached to the outside of the reactor, and this temperature was reported as pyrolysis operating temperature in this article. This outside temperature was maintained constant throughout the operation. Two condensers were installed to collect bio-oil in which the first condenser (70°C) was cooled through natural convection, whereas the second condenser was maintained at 0°C to condense vapors and aerosols escaped from the first condenser. The gases, vapors, and aerosols produced during the pyrolysis were condensed as liquid (bio-oil) using these two condensers attached to the tail end of the reactor. The bio-oil obtained from those condensers were mixed together to measure the total yield of bio-oil. Gas produced during pyrolysis (escaped from the second condenser) was vented to the atmosphere, and the char was collected after cooling the reactor to room temperature. At the end of the experiment (when the white fumes in the condenser disappeared), nitrogen gas was purged for 2 min to remove all the vapors from the reactor. A randomized experimental design was developed and experiments were carried out in triplicate at each temperature. All of the statistical analyses were done using one-way ANOVA at 95% confidence interval. Bio-oil and bio-char yields were calculated by measuring their weights at the end of each experiment, whereas the gas yield was determined from the difference (100 minus the sum of the weight of bio-oil and bio-char).

### 2.3. Bio-oil and Bio-char Analyses

Physical properties (pH, density, viscosity, water content, solid, ash, and higher heating value) of bio-oils produced at different temperatures were measured using the procedures described elsewhere (Thangalazhy-Gopakumar et al., 2010). The ash content and the heating value of bio-oil were determined as described in section 2.1. Ultimate analysis of raw bio-oil produced at 500°C was measured in a CHNS/O analyzer (Perkin Elmer model 2400, Shelton, CT, USA). Each measurement was carried out in triplicate and their average values were reported in this article. Bio-oil compounds were quantified using an Agilent GC/MS (7890/5975) with a DB-1701 column (30 m, 0.25 mm i.d., 0.25 mm film thickness). The detailed procedure for GC/MS analysis is document in the published literature (Thangalazhy-Gopakumar et al., 2010).

Physical properties of bio-char, such as moisture, ash, and higher heating value, were determined as stated in section 2.1.

## 3. RESULTS AND DISCUSSION

### 3.1. Biomass Characterization

Biomass properties play a major role in bio-oil production and in its properties. Physical and chemical properties of biomass used in this study are listed in Table 1. Cellulose, hemicelluloses, and lignin contents (by mass) were approximately 39, 22, and 29%, respectively. The cellulose content of this biomass was less than that of pinewood biomass (Thangalazhy-Gopakumar et al., 2011).

### 3.2. Effect of Temperature on Product Yield

Bio-oil, bio-char, and gas yields at different temperatures from UFB are presented in Figure 1. The ANOVA analysis showed that there was no significant change on bio-oil yield with respect to temperature in the range of 425 to 500°C. Most of the studies on woody biomass fast pyrolysis in auger reactors resulted in a lower amount of liquid yield (bio-oil) as compared to a fluidized-bed pyrolyzer. Typical bio-oil yield from an auger reactor is around 50–55 wt% (Bhattacharya et al., 2009). However, most of the recent studies with fluidized-bed reactors using different types of

TABLE 1  
Properties of Underutilized Forest Biomass Taken for Pyrolysis<sup>a</sup>

<i>Properties (Wet Basis)</i>	<i>Underutilized Forest Biomass</i>
Moisture content (wt%)	5.0 ± 0.3
Bulk density (kg/m <sup>3</sup> )	260
HHV (MJ/kg)	18.1 ± 0.3
Cellulose (wt%)	38.9 ± 0.1
Glucan	
Hemicellulose (wt%)	
Xylan	7.6 ± 0.2
Galactan	3.3 ± 0.0
Arabinan	2.1 ± 0.0
Mannan	9.3 ± 0.0
Extractives	1.5 ± 0.0
Lignin (wt%)	
Acid insoluble	28.2 ± 3.8
Acid soluble	0.8 ± 0.0
Ash content (wt%)	0.9 ± 0.1

<sup>a</sup>Values are means of repeated analysis and the numbers after ± are standard deviation.

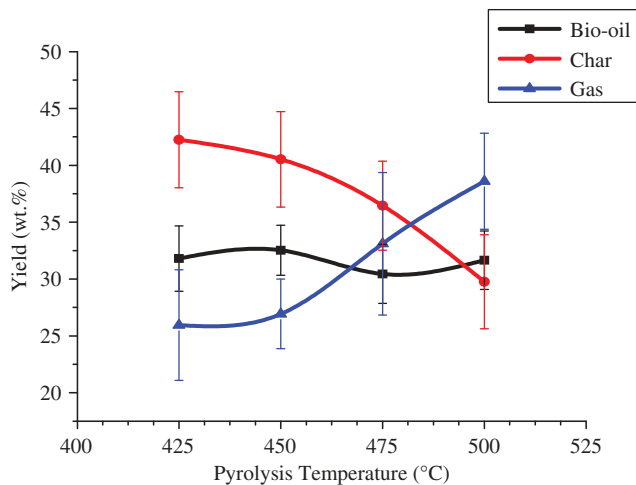


FIGURE 1 Product yield of underutilized forest biomass at selected temperatures.

biomass produced above 60 wt% bio-oil (Garcia-Perez et al., 2010). The current set-up produced only 30–35 wt% bio-oil from UFB, which was similar to liquid yield from a slow pyrolysis.

### 3.3. Effect of Temperature on Physical Properties of Bio-oil

There were some physical differences between bio-oils collected from the first and second condensers. Bio-oil collected from the first condenser had higher amounts of top phase (aqueous phase components) than that of the second condenser’s bio-oil. This study was focused on the properties of whole bio-oil and, therefore, bio-oils from both the condensers were mixed well. As bio-oil separates into different phases when stored for several days without any disturbance, the

whole bio-oil was mixed well before analyzing each property. Bio-oil was stored in a refrigerator just after their production and taken out during the time of analysis. Physical properties of the bio-oil produced from UFB at four different temperatures are summarized in Table 2. The table also shows corresponding values from the ASTM standard D 7544–09.

From this table, it appears that the density of the bio-oil decreased as the operating temperature increased but, statistically, there was no significant change. Bio-oil density reported in a previous literature (Garcia-Perez et al., 2010) was almost similar to the results from this study. Furthermore, temperatures investigated in this study did not have any influence on water content and HHV of bio-oil. Results were in agreement with the study from Thangalazhy-Gopakumar et al. (2010), where pinewood was used as a feedstock. A study from Oasmaa and Peacocke (2001) showed that the density of bio-oil is a strong function of its water content. Since water content was not influenced by the operating temperatures, there was no change in the density of bio-oil. On the other hand, pH and solid content of the bio-oil increased with the increase in temperature. However, the pH value of bio-oil obtained from UFB was higher than that obtained from pinewood (Thangalazhy-Gopakumar et al., 2010). The ash content of the bio-oil was higher when compared to the ASTM standard, and the reason behind this large number could be due to soil and sand particles (less than 1  $\mu\text{m}$  in size) entrained with the bio-oil vapor during the pyrolysis.

### 3.4. Ultimate Analysis of Bio-oil

The elemental analysis of bio-oil produced at 500°C showed that raw bio-oil had a carbon content of  $43.8 \pm 7.2\%$ , hydrogen content of  $7.6 \pm 0.4\%$ , and nitrogen content of  $0.7 \pm 0.5\%$ . Oxygen content was calculated from the difference as  $47.9 \pm 7.2\%$ .

Since UFB had not been used in previous studies, bio-oil's elemental composition was compared with the bio-oil from pinewood. Bhattacharya et al. (2009) reported carbon content greater than 50 wt%, and oxygen content less than 40 wt%. The current result is in-line with some of the earlier studies (Ji-lu, 2007; Wu et al., 2008) that have used as rice husk, saw dust, and cotton stalk as feedstocks.

### 3.5. Quantification of Bio-oil Components

Major quantified bio-oil components and their concentrations at different pyrolysis temperatures are given in Table 3. Different compounds, such as acids, ketones, anhydrosugar, furan, phenol, guaiacol, and syringol, were detected. The concentration of levoglucosan was decreased as the pyrolysis temperature increased from 425 to 500°C. This result was in-line with the previous study on switchgrass feedstock where low temperature favored the production of levoglucosan (He et al., 2009). However, the ANOVA analysis showed that the decrease in levoglucosan yield was not a significant decrease. An interest in industrial production of anhydrosugar from the fast pyrolysis of woody biomass has been there for the past 20 years. A rapid increase in phenol and cresol compounds was noticed when the pyrolysis temperature increased from 475 to 500°C. The increase in these compounds for the increase in pyrolysis temperature was significant. A similar result for phenols in bio-oils, irrespective to the type of biomass, was observed elsewhere (Thangalazhy-Gopakumar et al., 2010, 2011). A decrease in the concentration of guaiacol and isoeugenol compounds were noticed when the temperature rose to 500°C. The rapid increase in phenol compounds (from 475 to 500°C) can be mainly due to the thermal cracking of guaiacol compounds. Concentration of different compounds in bio-oil in this study was lower than the concentrations of the same compounds in bio-oil produced from pinewood using the same reactor (Thangalazhy-Gopakumar et al., 2010). The bio-oil collected from UFB was qualitatively similar to the bio-oil collected from other types of biomass. However, the quantification of different chemical

TABLE 2  
Physical Properties of Bio-oil Produced from Underutilized Forest Biomass at Various Temperatures<sup>a</sup>

Properties	Pyrolysis Temperature, °C				p-Value from ANOVA Test	ASTM Standard D 7544-09
	425	450	475	500		
Density, kg/m <sup>3</sup>	1,191 ± 16	1,185 ± 9	1,181 ± 10	1,175 ± 24	Not significant	1,100–1,300
pH	2.95 ± 0.06	2.97 ± 0.07	3.01 ± 0.05	3.08 ± 0.06	Significant	Report
Water, wt%	18.3 ± 1.65	18.04 ± 1.5	17.28 ± 1.31	17.23 ± 1.29	Not significant	30 max.
HHV, MJ/kg	19.59 ± 1.01	20.49 ± 0.59	20.20 ± 0.88	19.60 ± 1.00	Not significant	15 min.
Ash, wt%	0.85 ± 0.25	0.71 ± 0.18	1.01 ± 0.18	0.68 ± 0.15	Significant	0.25 max.
Solid, wt%	0.33 ± 0.14	0.42 ± 0.06	0.49 ± 0.09	0.49 ± 0.05	Significant	2.5 max.

<sup>a</sup>Values are means of repeated analysis and the numbers after ± are standard deviation.



TABLE 3  
Concentration of Bio-oil (wt%) Compounds and Their Relative Yield at Selected Temperatures

Compounds	Temperature, °C			
	425	450	475	500
Levogluconan	1.9 ± 0.2	1.8 ± 0.2	1.7 ± 0.5	1.6 ± 0.5
Furfural	0.2 ± 0.01	0.14 ± 0.07	0.15 ± 0.03	0.13 ± 0.03
Phenol <sup>a</sup>	0.02 ± 0.01	0.02 ± 0.01	0.03 ± 0.01	0.04 ± 0.02
(o/p) Cresol <sup>a</sup>	0.03 ± 0.02	0.04 ± 0.01	0.05 ± 0.02	0.07 ± 0.03
Guaiacol <sup>a</sup>	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.02	0.04 ± 0.01
cis/trans-Isoeugenol <sup>a</sup>	0.06 ± 0.01	0.06 ± 0.01	0.05 ± 0.02	0.03 ± 0.01

<sup>a</sup>Significant change in the yield with the increase in pyrolysis temperature at 95% confidence level in ANOVA analysis.

TABLE 4  
Physical Properties of Bio-char Produced at Various Temperatures<sup>a</sup>

Properties	Pyrolysis Temperature, °C				<i>p</i> -Value from ANOVA Test
	425	450	475	500	
HHV, MJ/kg	23.01 ± 0.56	23.65 ± 0.92	23.98 ± 0.5	25.59 ± 0.76	<0.0001
Ash, wt%	2.07 ± 0.26	2.74 ± 0.44	2.88 ± 0.67	3.36 ± 0.65	<0.0001
Moisture content, wt%	1.14 ± 0.36	0.56 ± 0.42	0.77 ± 0.39	0.95 ± 0.52	0.0234

<sup>a</sup>Values are means of repeated analysis and the numbers after ± are standard deviation.

compounds in bio-oil was comparable with the bio-oil obtained from slow pyrolysis (Branca et al., 2003).

### 3.6. Bio-char Analysis

Bio-char obtained from four different temperatures was characterized for heating value, ash content, and moisture, and the results are summarized in Table 4. From the statistical analysis, it was found that heating value, ash, and moisture contents of bio-char had shown a significant change with respect to the increase in pyrolysis temperature. The bio-char obtained at 500°C showed the maximum heating value of 25.59 MJ/kg.

## 4. CONCLUSIONS

Underutilized forest biomass was processed at selected temperatures (425, 450, 475, and 500°C) to produce bio-oil using an auger reactor. The study found that the yield of bio-oil was almost constant at different temperatures. On the other hand, both the bio-char and gas yields were significant with respect to the temperature. Selected physical properties of bio-oil produced at different temperatures were measured and compared with the ASTM standard, and it was found that almost all of the properties of bio-oil met the standard except the ash content. Chemical compounds identified in this study were lower than that of pinewood bio-oil, but had comparable yields with bio-oil from slow pyrolysis.

## ACKNOWLEDGMENTS

The authors are responsible for the opinions expressed in this paper and for any remaining errors.

## FUNDING

The authors would like to thank the United States Department of Agriculture (USDA)-Forest Service for funding this study.

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