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# Biofuels from Beech Wood via Thermochemicals Conversion Methods

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**Abstract** *In this study, characterization of Oriental beech wood (*Fagus orientalis*) with Turkish origin was investigated with aspect of structural, chemical, and thermochemical conversational properties. Liquefaction, supercritical fluid extraction, and pyrolysis of the samples were studied to obtain liquid fuel oils and chemicals. Beech wood was partly converted to liquefaction products in glycerol. The conversion products were 19.4, 32.3, and 64.6% by weight at 523, 543, and 563 K, respectively. The liquefaction yield sharply increased with increasing the temperature near critical temperature and after that. Ethanol is the best solvent for supercritical fluid extraction at lower temperatures. In the pyrolysis, increases of liquid yields are considerably sharp for all of the samples with increasing of pyrolysis temperature from 695 to 720 K. The highest increase of liquid yield was obtained from the beech wood sample with +0.063 mm particle size in the pyrolysis conditions. The maximum liquid yield was 36.3% at 720 K.*

**Keywords** beech wood, liquefaction, pyrolysis, supercritical fluid extraction

## Introduction

The components of biomass include cellulose, hemicelluloses, lignin, extractives, lipids, proteins, simple sugars, starches, water, hydrocarbons, ash, and other compounds. Two larger carbohydrate categories that have significant value are cellulose and hemicelluloses (holocellulose). The lignin fraction consists of non-sugar-type molecules (Demirbas, 2008).

Wood and other forms of biomass are one of the main renewable energy sources available and provide liquid, solid, and gaseous fuels. Animal wastes are another significant potential biomass source for electricity generation and, like crop residues, have many applications, especially in developing countries. Biomass is simply an organic petroleum substitute that is renewable (Garg and Datta, 1998). Biomass has been recognized as a major world renewable energy source to supplement declining fossil fuel resources (Ozcimen and Karaosmanoglu, 2004; Jefferson, 2006).

The technologies include a large variety of thermal and thermochemical processes for converting biomass by combustion, gasification, and liquefaction, and the microbial conversion of biomass to obtain gaseous and liquid fuels by fermentative methods. Liquefaction processes result in liquid product, which can be easily stored and transported and require lower process temperatures. Due to these advantages, it is becoming increasingly

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evident that liquid products offer more potential for the production of bio-based products than gas products and this is reflected in the rapid development of these processes and the large amount of research in this area (Mohan et al., 2006).

Biomass fast pyrolysis liquefaction has aroused great attention and interest, both at home and abroad, extensively in recent years. Furthermore, the problems and focus were summarized with some suggestions presented on upgrading and applications of bio-oil over the decades (Qi et al., 2007). The pyrolysis of biomass is a thermal treatment that results in the production of liquid (pyrolytic oil or bio-oil), gaseous, and solid (char) products. The pyrolysis of biomass has been studied with the final objective of recovering a bio-fuel with medium-low calorific power (Bridgwater et al., 1999; Raveendran and Ganesh, 1996; Babu and Chaurasia, 2003).

Oriental beech (*Fagus orientalis* Lipsky) belongs to the Beech family (*Fagaceae*) and is closely related to its European counterpart (*F. sylvatica* Lipsky) (Gömöry et al., 1995). It is a large tree and normal mean heights in Turkey are 30 m but it can reach heights of up to 50 m.

Branca and co-workers (2005a, 2005b) studied the thermal behavior of bio-oils obtained from conventional pyrolysis at temperatures of 700–950 K. These were compared to bio-oil formed by the updraft gasification of beech wood. At higher temperatures, heterogeneous combustion of secondary char occurred. Branca et al. (2003) characterized the liquids generated from the low-temperature pyrolysis of wood by GC/MS. Conventional beech wood pyrolysis was conducted at a temperature of 700–950 K, reproducing the conditions of interest in counter-current.

This study is devoted to obtaining liquid products from beech wood via liquefaction, supercritical fluid extraction, and pyrolysis processes. The yields of liquid products via these processes and reaction parameters on the products were discussed in this article.

## Experimental

The beech wood samples used in the experimental studies were taken from the Eastern Black Sea region in Turkey approximately 40° 39' northern latitude at an altitude of 900 m. The trees were 35–55 years old. Before experiments, the air-dried wood samples with 5% moisture were chipped and then ground in a Thomas-Wiley mill to pass between 0.063 and 0.250 mm screen opening.

For structural analyses, the wood samples were prepared according to TAPPI standard (TAPPI T 11 m-45). The percent lignin and percent extractives of the ground sample were determined. The ground sample was extracted with ethanol-benzene according to ASTM, and the lignin was determined as the insoluble residue after hydrolysis with 72% sulfuric acid.

The chemical analyses of the samples were carried out according to the ASTM D1103-80 and ASTM D1104-56 standard test methods.

Wood meal and anhydrous glycerol containing the appropriate amount of alkali ( $\text{Na}_2\text{CO}_3$ ) were put into a round bottom distilling flask with two cylindrical standard ground joint necks. To the flask was attached a Liebig condenser with two standard ground joints NS cones of 75° angle connecting tubes. The temperature was measured with a mercury-type thermometer (upper limit of reading being 673 K), which was attached to one neck of the distilling flask. Then the flask was immersed into a used vegetable oil bath. Products from wood meal passing into the condenser were collected in an Erlenmeyer flask at atmospheric pressure. The required liquefaction time of wood meal as described was about 15–20 minutes.

The liquid products from wood meal were fractionated into water solubles, water insolubles, and solid residue.

Experiments of supercritical fluid liquefaction were carried out in a 0.25 l autoclave. The temperature was measured with a thermocouple and controlled to an accuracy of  $\pm 3$  K. The sample was loaded via the bolt hole with M12 35  $\times$  15 into the autoclave, and the hole was plugged with a screw bolt before each run. The tubular reactor was inserted into an electrically-heated tubular furnace.

In a typical supercritical fluid extraction, 10.0 g of the sample and 100 g of solvent were fed to the 0.25 l autoclave. After completion of the extraction, the autoclave is cooled to room temperature. After each run, the gaseous products were captured in an Erlenmeyer flask. The rest of the oil and solids were removed from the autoclave by washing with solvent.

The pyrolysis experiments were carried out in a stainless steel tube reactor with a height of 95.1 mm, i.d. of 17.0 mm, and o.d. of 19.0 mm. Its total volume was about 21.6 mL. The ground sample was weighed for a run 1.00 g and pyrolyzed in the tube. Heat to tube was supplied from external electrical heater and the power was adjusted to give an appropriate heat-up time. The simple thermocouple (NiCr—constantan) was placed directly in the pyrolysis medium. For each run, the heater was started at 298 K and terminated when the desired temperature was reached.

The pyrolysis products from different heating rate runs were collected within three different groups as non-condensable gaseous products, condensable liquid products, and solid residue (bio-char). Following pyrolysis, the liquid products were collected in a series of traps maintained at about 273 K, and the organic part of the oil phase, which dissolved in benzene, was extracted in a rotary evaporator and the quantity of pyro-oil was established. The higher heating values (HHVs) of pyro-oil and bio-char from the samples in relation to the pyrolysis temperature were determined by bomb calorimeter according to the ASTM D2015 standard method.

Experiments were designed to investigate the effects of both the particle size and temperature of pyrolysis on yields of liquid and gaseous products and their characteristics. The temperature was maintained at 550, 600, 650, 700, 750, and 800 K, while the heating rate was 40 K/s. All yields were expressed on a dry and ash-free (daf) basis, and the average yields from three experiments were presented within the experimental error of  $\pm 0.3$  wt%.

## Results and Discussions

Table 1 shows the chemical and structural analyses of beech wood. The yields of fractions from the alkali liquefaction products of beech wood are given in Table 2. Table 2 shows that within the range of 553–573 K, beech wood was converted completely into a liquid product and the yield of total water insolubles was about 66% in the presence of 10% of sodium carbonate as alkali. At these conditions, the yields of non-condensed gaseous materials were almost negligible. Since water in the reaction medium has led to foaming, it was removed continuously from the medium.

Liquefaction in supercritical fluid was carried out in an autoclave at the critical temperature and the pressure of the solvent and it was observed that the yield of soluble material increases with increasing pressure.

As can be seen from Figure 1, temperature appeared to have no significant effect at low temperatures below the critical temperatures of solvents. Figure 1 shows that at temperatures lower than critical degree, the yield of liquid products is considerably low

**Table 1**  
Chemical and structural analyses of beech wood

Analysis	wt%
<i>Elemental analysis (dry ash free basis):</i>	
Carbon	49.5
Hydrogen	6.2
Nitrogen	0.4
Oxygen (by different)	41.2
<i>Structural analysis (dry ash free basis):</i>	
Hemicelluloses	31.2
Cellulose	45.3
Lignin	21.9
Alcohol/Benzene (1/1, v/v) extractives	1.6
<i>Proximate analysis:</i>	
Ash	0.4
Volatile matter	82.5
Fixed carbon	17.1

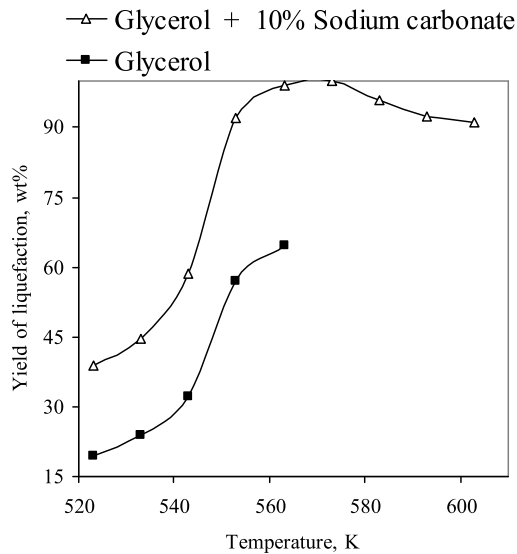
and the yields sharply increase with the increasing of temperature. The liquefaction yield sharply increased with increasing the temperature near critical temperature and after that. At temperatures greater than critical temperature, liquefaction yield slightly increased. Ethanol is the best solvent for supercritical fluid extraction at lower temperatures. According to the results, the yields obtained by supercritical fluid extraction are considerably higher than sub-critical conditions.

Figure 2 shows the plots for yield of liquid products from pyrolysis versus pyrolysis temperature for different particle sizes of beech wood. As can be seen from Figure 2, increases of liquid yields are considerably sharp for all of the samples with increasing of pyrolysis temperature from 695 to 720 K. The highest increase of liquid yield was obtained from the beech wood sample with +0.063 mm particle size in the pyrolysis conditions. The maximum liquid yield was 36.3% at 720 K.

Figure 3 shows the plots for yield of products from pyrolysis versus pyrolysis temperature for different particle sizes of beech wood. As can be seen from Figure 3, increases of the yield of gaseous products are considerably sharp for all of the samples

**Table 2**  
Yields of fractions from the alkali liquefaction products of beech wood

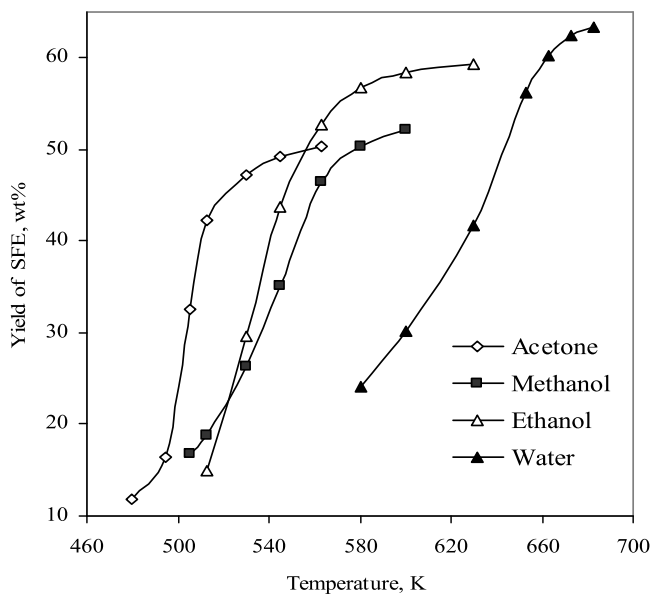
Product	Percent of used sample
Total water solubles	33.9
Total water insolubles	66.1
Tarry materials	38.1
Ether extractables	9.2
Benzene extractables	18.8



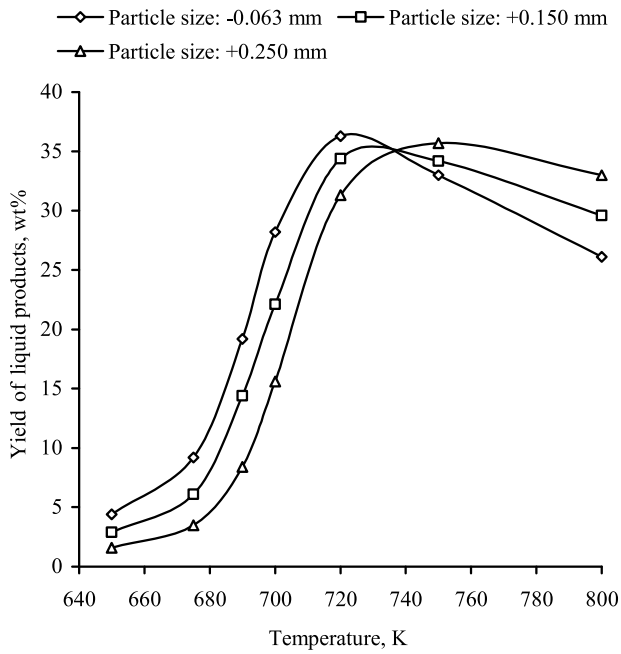
**Figure 1.** Plots for liquefaction yield of beech wood versus temperature in glycerol and alkali (10%  $\text{Na}_2\text{CO}_3$  of used sample) glycerol. Particle size: 0.063–0.250 mm.

at 695–730 K temperatures. From a comparison of Figures 3 and 4, while the yield of gaseous products continuously increases with increasing temperature, the yield of liquid products decreases after a determined pyrolysis temperature.

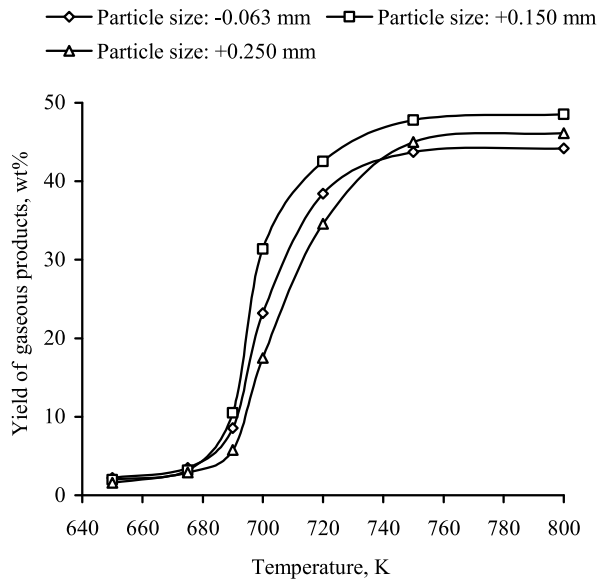
Thermogravimetric (TG) and differential TG studies of beech wood meal illustrated that wood decomposition began at 473 K, reached a maximum rate of mass loss at



**Figure 2.** Plots for liquefaction yield by supercritical fluid extraction (SFE) of beech wood.



**Figure 3.** Plots for yield of liquid products from pyrolysis versus pyrolysis temperature for different particle sizes of beech wood.



**Figure 4.** Plots for yield of gaseous products from pyrolysis versus pyrolysis temperature for different particle sizes of beech wood.

623 K, and continued to 773 K, illustrating the complex contributions of all the chemical constituents (Jakab et al., 2000).

Demirbas (2004) determined the high-heating values (HHVs) of biochar (33.2 MJ/kg) and oils (34.6 MJ/kg) from the pyrolysis of beech trunk barks. The effects of both the heating rate and pyrolysis temperature on bio-oil and char yields and their characteristics were investigated. A maximum pyrolysis oil yield of 36% was obtained at 700 K. However, by increasing the pyrolysis temperature from 700 to 800 K, the bio-oil yield decreased to 32.6 wt%.

Oriental beech trunk bark was pyrolyzed to obtain bio-char and pyro-oil for determining their calorific values. It was concluded that both the temperature and heating rate had a significant effect on both the yield of pyro-oil and bio-char resulting from pyrolysis of beech trunk bark (Demirbas, 2004).

The initial pyrolytic degradation reactions include depolymerization, hydrolysis, oxidation, dehydration, and decarboxylation (Zanzi, 2001; Effendi, 2004). The liquid fraction of the pyrolysis products consists of two phases: aqueous and non-aqueous. The aqueous phase contains a wide variety of organo-oxygen compounds of low molecular weight. Among the liquid products, methanol is one of most valuable products. The non-aqueous phase contains insoluble organics of high molecular weight (Demirbas, 2000; Maschio et al., 1992). This phase is called tar and is the product of greatest interest. Tar from wood is a very complex body, its composition varying with the kind of wood and method of preparation. The chief constituents are pyrocatechol, phenol, guaiacol, cresol, creosol, methyl-cresol, phlorol, toluene, xylene, naphthalene, and other hydrocarbons (Demirbas, 2000). The ratios of acetic acid, methanol, and acetone of aqueous phase were higher than those of the non-aqueous phase. Tar a viscous black fluid that is a byproduct of the pyrolysis of beech wood and is used in pitch, varnishes, cements, preservatives, and medicines as disinfectants and antiseptics.

Bio-oil from wood pyrolysis is typically a liquid, almost black through dark red brown. The density of the liquid is about 1,200 kg/m<sup>3</sup>, which is higher than that of fuel oil and significantly higher than that of the original biomass. Bio-oils typically have water contents of 14 to 33 wt%, which cannot be removed by conventional methods like distillation. Phase separation may occur above certain water contents (Demirbas, 2008).

The bio-oil formed at 725 K contains high concentrations of compounds, such as acetic acid, 1-hydroxy-2-butanone, 1-hydroxy-2-propanone, methanol, 2,6-dimethoxyphenol, 4-methyl-2,6-dimethoxyphenol, 2-cyclopenten-1-one, etc. A significant characteristic of bio-oils is the high percentage of alkylated compounds, especially methyl derivatives. As the temperature increases, some of these compounds are transformed via hydrolysis (Kuhlmann et al., 1994). The formation of unsaturated compounds from biomass materials generally involves a variety of reaction pathways, such as dehydration, cyclization, Diels-Alder cycloaddition reactions, and ring rearrangement. For example, 2,5-hexandione can undergo cyclization under hydrothermal conditions to produce 3-methyl-2-cyclopenten-1-one with very high selectivity of up to 81% (An et al., 1997).

## Conclusion

Oriental beech wood was subjected to thermochemical processes, such as liquefaction, supercritical fluid extraction, and pyrolysis to obtain liquid products. The liquefaction and supercritical fluid extraction processes relatively occur at low temperatures.

Oriental beech wood was liquefied in glycerol in the presence of Na<sub>2</sub>CO<sub>3</sub> as alkali. Alkali salts can lead to the formation of hydrolysis of macromolecules, such as cellulose



and hemicelluloses, into smaller fragments. In the liquefaction process, the amount of solid residue increased in proportion to the lignin content. The heavy oil content of the liquefaction products increased with increasing lignin content of biomass.

The supercritical fluid extraction is a promising method for recovery of chemicals and liquid fuels present in wood. Supercritical acetone, methanol, ethanol, and water have all been found to be effective solvents for the solubilization of wood lignin and cellulose.

Biomass pyrolysis is attractive because solid biomass and wastes can be readily converted into liquid products. These liquids, as crude bio-oil or slurry of charcoal with water or oil, have advantages in transport, storage, combustion, retrofitting, and flexibility in production and marketing. In wood-derived pyrolysis oil, specific oxygenated compounds are present in relatively large amounts. The liquid fraction of the pyrolysis products consists of two phases: aqueous and non-aqueous. The aqueous phase contains a wide variety of organo-oxygen compounds of low molecular weight.

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