Short Communication

Pyrolysis of hornbeam (*Carpinus betulus* L.) sawdust: Characterization of bio-oil and bio-char

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HIGHLIGHTS

- Slow pyrolysis of hornbeam sawdust residues was performed in a fixed-bed reactor.
- Bio-oil and bio-char were characterized with the various techniques.
- Both bio-oil and bio-char could be used as bioenergy sources.
- The HHV of bio-char reached the maximum value of 32.88 MJ kg^{-1}.

ARTICLE INFO

ABSTRACT

Slow pyrolysis of hornbeam (*Carpinus betulus* L.) sawdust was performed to produce bio-oil and bio-char. The operational variables were as follows: pyrolysis temperature (400–600 °C), heating rate (10–50 °C min^{-1}) and nitrogen flow rate (50–150 cm^3 min^{-1}). Physicochemical and thermogravimetric characterizations of hornbeam sawdust were performed. The characteristics of bio-oil and bio-char were analyzed on the basis of various spectroscopic and chromatographic techniques such as FTIR, GC–MS, 1H NMR, SEM, BET. Higher heating value, density and kinematic viscosity of the bio-oil with maximum yield of 35.28% were 23.22 MJ kg^{-1}, 1289 kg m^{-3} and 0.6 mm^2 s^{-1}, respectively. The bio-oil with relatively high fuel potential can be obtained from the pyrolysis of the hornbeam sawdust and the bio-char with a calorific value of 32.88 MJ kg^{-1} is a promising candidate for solid fuel applications that also contributes to the preservation of the environment.

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1. Introduction

The reserves of conventional fossil fuels have become limited in the present time, where the use of energy has been increasing faster than the world's energy generation. Sustainable and economic development requires safe and economic achievement to the energy resources to provide requisite and sustainable energy services (Yuan et al., 2015). The increase in the emission rates of greenhouse gases associated with fossil fuels drive global interest in renewable energy supplies, in particular energy derived from biomass (Chen and et al., 2015).

Energy from biomass is abundant, clean, and carbon dioxide neutral since a huge amount of biomass is produced every time through photosynthesis with solar energy using CO_2 and H_2O naturally. Biomass utilization as an energy source generates significantly less net CO_2 than that of fossil fuels since biomass

formation is a part of the carbon cycle in nature. Moreover, biomass presents additional advantages of lower sulfur and nitrogen contents than those of conventional fuels (Yu et al., 2014; Amutio et al., 2012).

Opportunities for renewable forms of energy production-hydro, wind, solar, geothermal and others-are abundant in Turkey. Among them, biomass energy is utilized less than others. Thousands of different plants grow in Turkey and these biomass sources can be evaluated for production of bioenergy. Hornbeams are typical tree species of the Northern Hemisphere. European hornbeam (*Carpinus betulus* L.) is the most common of the species and it is native to Europe, Anatolia and southeastern England. European hornbeam is a deciduous tree growing up to 20 m high and occasionally up to 30 m within 5–7 years that covers approximately 2×10^8 m^2 in Turkey (Hofmann et al., 2016; Öztürk et al., 2015; Akburak et al., 2016). Hornbeam can be considered as a potential source of biomass because of its low cost, easy availability and environmental sustainability. The utilization of this source of biomass would minimize the environmental impacts and are also sustain-

able based on current and future economic and social societal needs for Turkey.

Energy from biomass can be obtained via thermochemical processes such as gasification, pyrolysis and combustion. Pyrolysis is a thermal degradation of organic substances, especially the lignocellulosic residuals from agroforest and industrial production, under atmospheric conditions with a lack of oxygen into valuable products as liquid, solid and gaseous phases (Xiao and Yang, 2013).

Many other studies have been done to make bio-oil and bio-char for various applications using different precursors. Nevertheless, the search for ways to produce bio-oil and bio-char with excellent fuel properties, still presents a major challenge in this field. Aim of this paper was (i) to investigate the pyrolysis of hornbeam sawdust under different conditions; (ii) to determine the suitable experimental parameters to achieve maximum bio-oil yield; and (iii) to characterize the bio-oil produced under suitable pyrolysis conditions using different spectroscopic and chromatographic methods to evaluate if the bio-oil can be valorized as fuel or chemical feed stocks. The bio-char was also analyzed to investigate its physicochemical properties.

2. Materials and methods

Hornbeam (*Carpinus betulus* L.) sawdusts (HS) have been taken from the residues of furniture factories around the city of Mersin, Turkey. Prior to use, the biomass sample was air dried for fixed-bed pyrolysis experiments. Proximate analysis of HS was carried out according to the American Society for Testing and Materials (ASTMs) Standard Test Methods. Ultimate analysis of the HS, bio-oil and bio-char was performed using a LECO CHNS 932 Elemental Analyzer to quantify the carbon (C), hydrogen (H) and nitrogen (N) contents. Oxygen (O) content was calculated by difference. Higher heating value (HHV) of HS, bio-oil and bio-char was tested with a GALLENKAMP Auto Adiabatic Bomb Calorimeter (ASTM D 240). Thermal behavior of HS residues was examined using Perkin Elmer Diamond thermogravimetric analyzer.

2.1. Experimental procedure

Samples of 15 g of HS were loaded into a 316 stainless steel-fixed bed reactor. The reactor was heated by an electric furnace. The experiments were performed in three series. For the first group of experiments, the fixed bed reactor loaded with hornbeam samples was raised to temperatures ranging from 400 to 600 °C at a rate of 40 °C min^{-1}. After reaching the final temperature, the furnace temperature was then kept at the final pyrolysis temperature for 30 min before cool down. The volatile pyrolysis products passed through a series of traps within a mixture at about 0 °C fixed up by ice and water to cool down into liquid product and then the condensed liquid product was recovered by washing with dichloromethane (DCM). Furthermore, non-condensable gaseous products that were simply left out of traps have been observed using a soap film. The obtained liquid product consisted of two phases, oil phase that settles at the bottom and aqueous phase that forms a top layer, was separated by a separating funnel. The oil phase was firstly passed over dry powder of sodium sulfate, and then the solvent was separated from oil phase under vacuum to obtain bio-oil by a rotary evaporator. The solid product remained in the reactor (bio-char) was removed after cooling and weighed. The yield of gas product was calculated by a difference: gas product yield = 100 − (liquid product yield + bio-char yield). The second group of experiments was performed at the pyrolysis temperature of 550 °C with five heating rates of 10, 20, 30, 40 and 50 °C min^{-1}. The last group of experiments were studied at sweep gas (N_2) flow rates of 50, 100 and 150 cm^3 min^{-1} at pyroly-

sis temperature of 550 °C and heating rate of 30 °C min^{-1}, based on the conditions of the first two steps that gave the highest bio-oil yield. All the yields were calculated on a dry ash free basis and the average yields of three experiments were presented within the experimental error of <±0.5 wt%.

2.2. Characterization methods of bio-oil and bio-char

The following characterization techniques were run on the bio-oil obtained in the highest yield at the pyrolysis temperature of 550 °C, heating rate of 30 °C min^{-1} and sweep gas flow rate of 100 ml min^{-1}. The bio-char obtained at the same conditions was also characterized to observe the changes in the properties of its structure.

Density of the bio-oil was measured using 10 ml pycnometer (ASTM D 369). The kinematic viscosity of the bio-oil was measured with KOEHLER, K-23378 Model viscometer (ASTM D 445). Detailed information about liquid column chromatography of the bio-oil can be found in the literature (Sensoz et al., 2006; Moralı and Şensöz, 2015). The functional group analyses of the bio-oil and the bio-char were achieved using FTIR (Perkin-Elmer 100 Model) in the range of 650–4000 cm^{-1} wavenumbers. The ^{1}H-NMR (Proton Nuclear Magnetic Resonance) spectrum of the bio-oil was obtained to determine the percentage of the hydrogen types using a Bruker AVANCE instrument. The chemical compounds of the n-pentane eluate of the bio-oil were analyzed using a 6850 Agilent HP gas chromatograph connected to a 5975 Agilent HP MS.

The surface morphology of the bio-char was analyzed using a scanning electron microscope (SEM, JEOL-JMS-5600 LV). The surface area of the bio-char was determined using N_2-BET (Quantachrome, Autosorb 1C). Nitrogen was used as the adsorptive gas at 77 K. Prior to gas adsorption measurements; the analysis involved outgassing the bio-char at 300 °C for 8 h using Quantachrome Flovac Degasser.

3. Results and discussion

3.1. Characteristics of raw material

The main characteristics of HS residues including the results of proximate, ultimate and component analyses are given in Table 1. Fig. 1 shows the TG-DTG curves of the HS. TG analysis of the biomass sample indicated that approximately 6.92% mass loss

Table 1
Main characteristics of hornbeam sawdust.

Characteristics	Standards	Hornbeam Sawdust
Moisture content (wt%)	ASTM D2016	8.78
Proximate analysis[a] (wt%)		
Volatiles	ASTM E 872-82	78.14
Ash	ASTM D1102-84	0.45
Fixed carbon[b]	By difference	12.63
Ultimate analysis[a] (wt%)		
Carbon		45.18
Hydrogen		6.59
Nitrogen		–
Oxygen[b]	By difference	48.23
Empirical formula	Calculation	$CH_{1.75}O_{0.80}$
H/C molar ratio	Calculation	1.75
Component analysis[a] (wt%)		
Cellulose	TS 4431	51.46
Hemicellulose[b]	By difference	11.54
Lignin	ASTM D 1106-96	28.00
Extractive	ASTM D 1105-56	9.00
HHV (MJ kg^{-1})	ASTM D 240	20.61

[a] Weight percentage on dry basis.
[b] By difference.