

# Production and Characterization of Biochars from Torrefaction of Biomass

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## Abstract

Effects of torrefaction process on properties of biomass fuel were investigated using three biomass species including olive milling residue (OMR), *Rhododendron* (RH), and ash tree (AT). The properties of these biomasses were evaluated considering proximate and ultimate analyses as well as higher heating value (HHV). Torrefaction of milled samples was implemented in a horizontal tube furnace by simply heating of biomasses from ambient to temperatures of 200, 250, and 300°C at a heating rate of 10°C/min. The biochars obtained from this thermal treatment process were also tested by the methods applied to the parent biomass species. Torrefaction-related improvements in the fuel properties were interpreted. That is, increasing torrefaction temperature led to regular increases in the HHV in OMR and the highest HHV (6065 kcal/kg) was gained at 300°C. Whereas, torrefaction at 250°C was seen optimum for *Rhododendron* since torrefaction at 300°C had a detrimental effect on HHV. Besides, increase in carbon contents and reduction in oxygen contents were determined. Burning characteristics of the biochars were also studied using thermal analysis technique. It was concluded that torrefaction is an efficient method to upgrade the fuel properties of biomass and the biochars from which have superior characteristics compared to the parent biomasses.

**Keywords**—Biochar, Biomass, Fuel upgrade, Torrefaction

## Introduction

Biomass is a CO<sub>2</sub>-neutral fuel that is renewable and sustainable along with having very huge global potential [1]. Every types of materials except fossil fuels that have C, H, and O contents can be regarded as biomass. From this point of view, very wide range of materials such as MSW (Municipal Solid Wastes), industrial wastes, agricultural residues, grasses, algae, etc. are defined as biomass. Efficient use of biomass in power generation and production of biomass-based biofuels can mitigate the greenhouse gases (GHG) and reduce dependency on fossil fuels [2]. CO<sub>2</sub> emitted from burning of biomass is almost equivalent to CO<sub>2</sub> captured by fresh biomass during photosynthesis and therefore it does not contribute to the net increase in greenhouse gases in atmosphere. There are also other beneficial effects of biomass energy use such as employment creation and pollutant reduction. That is, a number of biomass species especially woody ones have very low sulfur content compared to coal and they do not lead formation of serious SO<sub>x</sub> emissions.

However, most of the biomass materials do not compete with fossil fuels in terms of energy content [3]. High moisture content and high volatile matter yields of biomass make it relatively low calorific fuel and it is very serious lack of biomass over fossil fuels. In fact, woody biomass species are mainly comprised of three major ingredients such as cellulose, hemicellulose, and lignin. All of which are highly rich in oxygen content. High oxygen content not only lowers the calorific value of biomass but also enhances the thermal reactivity in any thermal process including combustion, gasification, pyrolysis, carbonization, etc.

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This high reactivity inevitably requires taking special precautions during handling of biomass since the stability of a thermal process is usually affected negatively from high reactivity of fuel. Utilization of biomass in existing energy systems designed for coal usually creates serious problems such as low yield of energy production, flame instability, and combustion at low temperatures. In particular, co-combustion systems where biomass and coal burn simultaneously suffer from segregation of coal and biomass particles that have different reactivity. The reason behind this fact is that the ratio of volatile matter to fixed carbon is higher in biomass compared to coal and accordingly burning of biomass initiates and ends at low temperatures. Besides, the bulk density of biomass is generally low and it brings difficulty in transportation and storage [4]. Therefore, transportation of biomass to long distances is uneconomic in most cases. These negative aspects of biomass can be overcome by thermal pretreatments that upgrade the fuel properties [5]. That is, torrefaction is the most suitable thermal process in which biomass is heated up to 300°C under non-oxidizing conditions to avoid burning of the material [6]. Hemicellulose that is highly rich in oxygen leads the formation of excessive amounts of volatiles. Based on this fact, hemicellulose can be easily degraded with this thermal pretreatment, while cellulose and lignin are not affected seriously. That's why most of the calorific value of biomass can be recovered after torrefaction process. The biomass remained from torrefaction is called as "biochar" that has considerably lower contents of moisture, volatile matter, and oxygen compared to the parent biomass [7]. Accordingly, carbon content and the calorific value of biochar increase to the level which is almost comparable with that of coal. Moreover, hydrophilic nature of untreated biomass that leads decay in structure is mostly eliminated and the surface properties of biochar turn into hydrophobic character upon torrefaction [8].

In this study, several biomass species were subjected to torrefaction process and the variations taken place in properties of these biomasses were investigated comparing the fuel characteristics of the parent samples and their biochars.

## Materials and Methods

Three different biomass samples, olive milling residue (OMR), *Rhododendron* (small shrubby tree with bell-shaped flowers), and ash tree (timber tree), were chosen for this study. All of these biomass species are highly abundant in Turkey. These samples were first chopped and milled to a particle size lower than 250 µm. Proximate analysis was carried out according to ASTM standards, while Leco TruSpec® CHN ultimate equipment with Leco TruSpec® S module was used to perform the ultimate analysis. HHV (higher heating value) of the samples was determined by IKA C2000 calorimeter. On the other hand, determination of the contents of the macromolecular components such as cellulose, lignin, hemicellulose as well as extractives was performed through wet analytical methods. For this, benzene/ethyl alcohol extraction method was applied to remove the extractives according to ASTM D1105 procedure. The extracted bulk was then used for determination of (cellulose + hemicellulose) and lignin contents. Namely, Wise's chlorite procedure [9] and van Soest method [10] were applied for isolation of (cellulose + hemicellulose) or lignin contents from the extracted bulk, respectively. All the tests were repeated several times to assure the repeatability of the experimental data and the mean values of the results were taken unless they are not deviated more than 5%.

Torrefaction experiments were implemented in a horizontal tube furnace by heating milled samples under nitrogen atmosphere from ambient up to temperatures of 200, 250, and 300°C at a constant heating rate of 10°C/min. For this, a horizontal tube furnace containing a silica tube with a diameter of 15 cm and a length of 72 cm was used. The radiation zone where heating is applied is just in the center of the silica tube and has a length of 5 cm. A PID controller performs the temperature control of the furnace. For each experiment, Approximately 10 g of milled biomass was put into silica crucibles and then the crucible was placed through the radiation zone of the cold furnace. Oxygen was purged out of the system by nitrogen flow, and then temperature was increased from ambient to the mentioned temperatures with a heating rate of 10°C/min under nitrogen flow at 100 mL/min, and the sample was kept at these final temperatures for 60 min in order to get the torrefied biomass (biochar). Torrefaction-related variations in the fuel properties were interpreted. Burning tests were done using TA Instruments SDT Q600 model thermal analyzer.

## Results and Discussion

Analysis results of the biomass samples are given in Table 1. Based on data given in Table 1, it is likely to mention that all of these samples are rich in cellulose and hemicellulose, while lignin contents are relatively low.

Accordingly, volatile matter yields are disproportionally higher than fixed carbon contents. Furthermore, ash tree is very poor in ash yield that is a superior nature of this sample over the others.

Table 1. Analysis Results of Biomass Samples (as received basis)

	OMR	RH	AT
Cellulose + Hemicellulose (%)	57.4	85.0	77.4
Lignin (%)	19.9	11.7	15.6
Extractives (%)	22.7	2.7	7.1
Moisture (%)	4.0	5.2	7.6
Volatile Matter (%)	80.1	78.9	80.4
Ash (%)	7.3	8.6	1.1
Fixed Carbon (%)	8.6	7.3	10.9
HHV (kCal/kg)	4869	4441	4117

Table 2 shows the proximate and ultimate analysis results of biochars. Comparison of the analysis results of biomasses and biochars reveals that some reductions occur in moisture and volatile matter contents as torrefaction temperature increases. Meanwhile, fixed carbon content increases that leads improvement in HHV. Since HHV is the most significant parameter that defines the quality of a fuel, it can be concluded that apparent improvements in the fuel quality of biomass can be achieved through torrefaction process. Concerning HHV, torrefaction temperature of 300°C are optimum for OMR and AT, while 250°C shouldn't be exceeded in case of RH since some reduction occurs when temperature is increased to 300°C. Being relatively poor in lignin content may be attributed to the reduction in heating value of the biochar since lignin is heat resistant ingredient in sample and hemicellulose rich materials undergo relatively larger destruction.

Table 2. Proximate and Ultimate Analyses Results of Biochars (%)

Sample	M <sub>ar</sub>	VM <sub>ar</sub>	Ash <sub>ar</sub>	FC <sub>ar</sub>	C <sub>daf</sub>	H <sub>daf</sub>	N <sub>daf</sub>	S <sub>daf</sub>	O <sub>daf</sub>	HHV (kCal/kg)
OMR200	3.0	77.6	10.9	8.5	59.4	7.5	1.2	0.6	31.3	4647
OMR250	3.3	73.6	11.6	11.5	64.0	7.7	1.6	0.3	26.4	5306
OMR300	3.0	57.6	26.3	13.1	85.7	8.4	2.2	0.4	3.3	6065
RH200	4.4	80.9	0.4	14.3	51.0	6.3	0.1	0.3	42.3	4618
RH250	3.5	77.9	0.5	18.1	53.6	6.3	0.2	0.3	39.6	4790
RH300	4.4	64.0	1.4	30.2	61.4	6.1	0.3	0.4	31.8	4632
AT200	2.6	84.0	1.6	11.8	n/a	n/a	n/a	n/a	n/a	4436
AT250	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	4571
AT300	4.2	69.3	0.4	26.1	57.5	5.8	0.4	0.3	36.0	5272

ar: as received      daf: dry-ash-free      M: moisture      VM: volatile matter      FC: fixed carbon

Effects of torrefaction temperature on burning characteristics of biochars were evaluated considering DSC curves derived from thermal analysis. Figure 1 illustrates DSC curves of RH biochars. It is apparent from these DSC curves that some enhancements in the heat flows during burning of the biochars took place as a function of torrefaction temperature. That is, torrefaction carried out at 300°C showed the highest heat flows. This confirms that torrefaction is capable of producing promising solid fuels in terms of energy giving characteristics during burning.

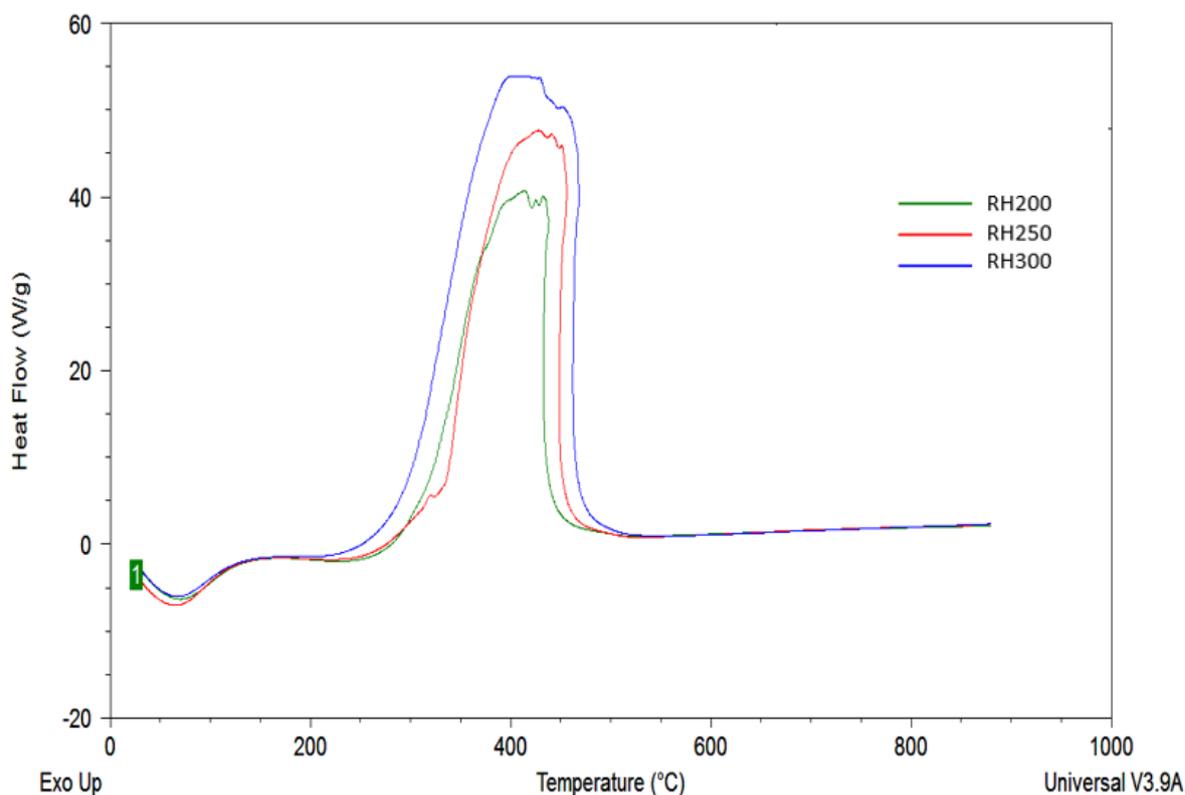


Fig.1. DSC Curves for RH Biochars

## Conclusions

Torrefaction method applied to the biomass materials led to significant variations in composition and burning characteristics. Comparison of the properties of biochars and untreated parent biomasses indicated that the ratio of volatile matter to fixed carbon reduced and HHV increased. That is, the HHVs of the biochars are almost comparable with those of high rank coals. Besides, high oxygen contents of biomass that is typical characteristics of these materials can also be reduced. This means significant improvements in the fuel properties of biomass through torrefaction. On the other hand, heat flows during burning of the biochars showed that increasing torrefaction temperature caused increase in the heat flows. This confirms that energy intense fuels can be produced from ordinary biomass species thanks to applied thermal pretreatment.

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