

Torrefaction and Hydrothermal Carbonization (HTC) of Dead Leaves

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ABSTRACT

Torrefaction and hydrothermal carbonization (HTC) are productive methods to reclaim energy from lignocellulosic biomass. The hydrophobic, homogenized, energy dense and carbon rich solid fuel can be obtained from torrefaction and hydrothermal carbonization. Dead leaves were carbonized in a stainless steel reactor of volume 200 ml with torrefaction (250-270°C) for 120 minutes and hydrothermal carbonization (200-250°C) for 30 minutes, with mass yield solid fuel ranging from 57-70% and energy content from 16.81 MJ/kg to 22.01 MJ/kg compared to the biomass. The char produced from torrefaction process possess high energy content than hydrothermal carbonization. The highest energy yield of 89.96% was obtained by torrefaction at 250°C. The energy densification ratio fluctuated in between 1.15 to 1.30. On the basis of pore size distribution of the chars, the definition of the International Union of Pure and Applied Chemistry (IUPAC) was used as a classification standard. The pore diameter was ranging within 11.09-19 nm which play important role in water holding capacity in soil. Larger pores can hold water and provide passage for small pores. Therefore, it can be concluded that high pore size char can be obtained by HTC process and high energy content char of 22.01 MJ/Kg with 34.04% increase in energy can be obtained by torrefaction process.

Keywords : Torrefaction, Hydrothermal carbonization, Char, Energy

1. Introduction

In current energy demand the world is suffering from two key challenges: energy supply and sustainability. Fossil fuel reserves are getting limited and their worst environmental impacts boost the use of biomass, which is the most abundant energy resource Toufiq et al. (2013). The socio economic development of any country is greatly dependent on its self-sufficiency in energy sector. The Worldwide fuel needs are keep increasing at fast rate (29.75 billion barrels oil in year 2011 and projected to increase about 34.90 billion barrels in 2030). This rapid increase in primary energy consumption has magnified concerns about the environmental consequences of fossil fuel extraction and use Luterbacher et al. (2009). In the past, biomass has been the fourth largest source of energy in the world with 10-14% of total energy consumption, with coal by 12-14%, natural gas by 14-15%, and electricity by 14-15% (Mafakheri and Nasiri, 2014). After the nuclear disaster in Japan, Germany decided

to abandon all its nuclear reactor till 2022 and would like to achieve the energy demand by other forms of energy like natural gas, wind, solar, coal, biomass and hydroelectric Oliveira et al. (2013). The world largest solar farm named as Ivanpah Solar Electric Generating System (ISEGS) in Mojave Desert of California opened early this year. This solar plant can provide energy to 140,000 homes in an hour. Furthermore it can reduce carbon dioxide emissions to 400,000 tons per year. The bioenergy is considered to be an effective way to solve the present energy crisis and other related environmental problems (Zhang and Changfu, 2013). Biomass includes wood, municipal and industrial waste, forest and agriculture residue as an upcoming alternative fuel for coal. Biomass in rural areas is primarily used in unscientific way for heating and cooking. Nevertheless the biomass usage in an industrial sector is an utter demanding Basu et al. (2014). If a biomass can provide a large quantity of the world's energy supply, then dedicated crops must be cultivated for energy purposes McKendry et al. (2002).

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Received : 2014. 10. 13 Reviewed : 2014. 10. 24 Accepted : 2014. 10. 24

Discussion until : 2014. 12. 31

Like different other countries in the world, South Korea also generate power from different resources. The major source of energy generation in Korea is coal followed by nuclear. According to Korean energy economic institute, in year 2011 about 200,893 gwh of energy was produces from coal and 154,723 gwh from nuclear reactor. Presently about 23 reactor are operating in Korea which contribute about 45% of South Korea total energy generation capacity Young-Sung et al. (2012). In recent year the energy generation from alternative means rose dramatically in Korea. The biomass energy obtained from agriculture and forest residue worldwide has potential of approximately 30 EJ/yr, whereas the demand of worldwide energy is over 400 EJ annually. Despite a small land Korea has 64% of a country under forest. Seoul a capital city South Korea generate about 600 tons of leaves in autumn season. Fallen leaves are recycled; few are forwarded to incinerator while some are buried in landfill. Biomass contains various amounts of hemicellulose, cellulose and lignin. A comparative proportion of lignin and cellulose are the determining the factors in identifying the energy crop (McKendry et al. (2002). Lignocellulose is the main component of plants which provide structure and present in roots, stalks and leaves Nanda et al. (2013).

Several researchers indicated that direct combustion of biomass is not so satisfying because of some inborn drawback of biomass which includes high oxygen, high moisture content and high alkaline heavy metals Khan et al. (2009). Moreover biomass possesses low bulk densities which are responsible for its low volume base heating value. Therefore energy recycling from biomass has received more attention because it provides large reduction in volume, hazard and heavy metals controlling. Direct incineration causes various problems like hard to ignite, incomplete and unstable combustion, large amount of gaseous pollutant and some secondary pollutants like photochemical smog, green house emission acid rain and ozone depletion Demibas A (2005). Disposal methods like landfill is responsible to emit methane, which has 20-25 times higher effect on global warming than CO₂ (Nahman and Lange, 2013).

Converting biomass into char is the paramount way to produce reasonable energy Singh et al. (2014). There are a minimum two different thermal carbonization processes, namely as dry torrefaction and wet torrefaction Yan et al.

(2009). Dry torrefaction is also known as mild pyrolysis, in which biomass is treated in an inert gas environment which take place at temperature range of 200-300°C. The solid and the gas are the byproduct of dry torrefaction process. About 60-80% of mass and 70-90% of energy value can be obtained as compare to raw biomass Lynam et al. (2011). The main principle of torrefaction process is to remove oxygen and enrich carbon in a solid product. After torrefaction the biomass has lower O/C ration contrast to original biomass Stelt et al. (2011). In torrefaction process, hemicellulose in biomass depolymerize, which result in releasing volatiles of low energy values and as a result the remaining solid has a high energy density Basu et al. (2014). A char produced by torrefaction process is known as torrefaction char.

In comparison, wet torrefaction which is also called as hydrothermal carbonization (HTC), use hot water for the carbonization of biomass results in three products: solid, liquid and gas. The temperature range for HTC is 200-260°C. The HTC mass yield is about 55-90% and the energy value of about 80-95%, while 10% of gas produces as compare to biomass. The aqueous solution obtain from wet torrefaction mainly contains acetic acid, sugar and other organic acids (Yan et al. 2009; Kobayashi et al. 2008). The solid product obtained from wet and dry torrefaction carbonization exhibit high energy value and high energy density Prins et al. (2006). The char produced by HTC process is known as HTC char.

Torrefaction process contains decarboxylation, demethoxylation, dehydration, decarbonylation, condensation and aromatization reactions. Decomposition of specific compounds can also be characterized by temperature. Hemicellulose mostly decomposes between 200 and 400°C, while cellulose decomposes between 300 and 400°C. On the other hand lignin decomposes between 180-600°C, which is the most stable component. In comparison during HTC process hydrolysis, decarboxylation, dehydration, recondensation and aromatization reactions take place. Nevertheless the HTC of biomass is initiated by hydrolysis, which exhibits lower activation energy than most torrefaction decomposition reactions. In HTC process lignin decomposes between 180-220°C, hemicellulose between 180-200°C and cellulose approximately above 220°C. Both torrefaction and HTC reactions are exothermic reactions. The amount of heat released is

dependent on the biomass used, residence time and mainly on temperature. In both carbonization processes the char yield decreases with increase in reaction temperature and significant amount of liquid by products are formed in HTC process Libra et al. (2011).

The overarching objective of this study was to (i) convert dead leaves into solid char by HTC and torrefaction process at different temperatures and retention time, (ii) compare the thermal properties of the char with lignite coal (iii) examine the physical and chemical composition of the produced char by HTC and torrefaction processes (iv) analyze the characteristics of char for water holding capacity and pore size.

2. Material and Methods

2.1. Biomass

Mixtures of different leaves in autumn season were collected from different locations in Seoul. These leaves were mixed thoroughly and grinded to acquire size less than 2 mm. All the grinded leaves were placed in oven for 24 hours at 105°C prior to carbonization process Lui, and Balasubramanian (2012).

2.2. Dry Torrefaction

After drying of the grinded leaves in an oven for 24 hours at 105°C as a preliminary treatment to completely eliminate the moisture content from biomass, the dried biomass of 7 g was placed in a stainless steel reactor (200 ml) for dry torrefaction. Dry torrefaction was carried out at different temperatures ranging from 250-270°C with residue time for 120 minutes. After the isothermal process, the reactor was immersed in a water tub for rapid cooling and solid samples were collected and stored for further analysis.

2.3. Hydrothermal Carbonization

HTC of dead leaves was also performed in stainless steel reactor (200 ml). Biomass of 7 g and 35 ml of hot deionized water (1 : 5 w/v) was loaded into a reactor and carbonized at different temperatures ranging 200-250°C. The retention time was fixed for 30 minutes. Prior to carbonization reaction, the biomass was manually mixed with hot deionized water to achieve proper wetting. After carboniza-

tion reaction the reactor was cooled rapidly by placing it in water tub. Solid and liquid products were separated by vacuum filtration. The solid product was rinsed by acetone and was dried in oven for 2 hours at 105°C. All samples were stored for further analysis.

2.4. Analytical Methods

The solid samples went through pH, Electronic conductivity (EC), yield, elementary analysis, ash content, surface area, cation exchange capacity (CEC), energy yield, energy densification ratio and energy content.

The pH and EC both were measured at the same time using digital meter. 1 g of solid sample was added in a 20 ml of de ionized water. This solution was equilibrated for 1.5 hours before analysis. The solid product yield was then extracted from amount of biomass. Elementary analysis like C, H, N, S and O were measured by using Thermo Electron Flash EA 1112. The solid samples were weighted and muffled in a tin solid capsule and was placed into reactor for oxidation/reduction reaction. The temperature of elementary analysis was between 900 and 1000°C. The ash content of solid samples was quantified by weight loss after inserting them in the furnace for 3 hours at 600°C 15 Guo and Rockstraw (2007). The ash content was achieved and presented in percentage of total solid sample weight. The surface areas of all the solid samples were examined by using nitrogen BET (Brunauer-Emmett-Teller) adsorption method Lee et al. (2013). BET equation was to calculate surface area of all samples. Average pore diameter with pore volume was also explored. Sodium chloride, ammonium acetate and ethanol replacement methods were used to measure the CEC of all solid samples Gaskin et al. (2008). Ammonium acetate solution of 20 ml was centrifuged in 1 g of solid sample for 10 min. The solid and liquid products were sunder by vacuum filtration. After filtration solid sample was immersed in sodium chloride solution of 20 ml and was re filtered. The solution was used for analysis. CEC was measured my Liquid Kjeldahl. The energy content of solid sample was determined by using CAL2K advance bomb calorimeter. The solid sample was placed into bomb calorimeter and was combusted in the presence of oxygen. The energy densification can be interpreted as the ratio of energy content of char and biomass while energy yield is

the cross product of yield of char with energy densification ratio.

3. Results and Discussion

HTC and Dry torrefaction of dead leaves were carried out at different temperatures. All the analytical experiments were performed in triplicate and mean values were extracted. All the physical properties of solid samples are given in Table 1. Higher carbonization temperature led to higher value of pH in solid product Yuan et al. (2011). The biomass was having pH of 4.34 which increased to 5.45 at 250°C for HTC pretreatment, while in torrefaction pH was the highest of 5.70 at 250°C and started to decrease on further increase in temperature. There was a sharp fall in the EC value from the biomass of 1893 us/cm to 747 us/cm at 250°C in HTC process, while in torrefaction EC values were much higher than HTC slightly lower than actual biomass. The decrease in CEC value with increase in temperature is because of disappearance of acidic functional group Gaskin et al. (2008). The CEC values started to decrease when raw material was heated. There was CEC 37.35% decrease in overall values in HTC process, furthermore

there was 43.4% decrease when treated in dry torrefaction process. The ash content started to increase in both processes and highest of 19.55% was obtained when carbonized in dry torrefaction process at 270°C. In both pretreatment, rise in temperature causes decrease in mass yield. In HTC process mass yield was 70.98% at 200°C while the lowest was of 57.39% at 250°C, on the other hand in torrefaction process the maximum yield was of 69.20% at 250°C and minimum was of 59.8% at 270°C. So it can be concluded that mass yield of torrefaction is more successful than HTC at 250°C.

Water holding capacity of the soil can be increased dramatically if the solid char is being added to soil. Limited amount of research is available on the water holding capacity of biomass Karhu et al. (2011). Solid char is a kind of porous media which can hold the water in its pores and afterward increase the water content of the soil, while on the other hand char added to the soil will attach to other soil constituents and will improve the structure of the soil, which in return increase the soil water holding capacity. The main factors that influence the water holding capacity are; total pore volume, surface functional groups, surface area and porosity structure. Table 2, shows the surface area BET

Table 1. Physical properties of char

Pretreatment	Temperature (°C)	pH	EC (us/cm)	CEC (meg/100)	Ash Content (%)	Mass Yield (%)
Biomass		4.34	1893	249.5	11.08	100
Hydrothermal Carbonization (HTC)	200	4.97	810	162.9	13.64	70.98
	230	5.13	857	202.7	11.08	63.43
	250	5.45	747	156.3	17.46	57.39
Torrefaction	250	5.70	1565	155.2	18.24	69.20
	260	5.18	1849	145.7	19.01	65.5
	270	5.38	1725	141.1	19.65	59.8

Table 2. Surface area, pore volume and pore diameter

Pretreatment	Temperature (°C)	BET (m ² /g)	Pore Volume × 10 ⁻³ (cm ³ /g)	Pore Diameter (nm)
Biomass		1.37	1.45	8.26
Hydrothermal Carbonization (HTC)	200	1.49	7.08	19.00
	230	1.39	5.04	14.45
	250	2.09	6.99	13.38
Torrefaction	250	0.71	1.8	10.53
	260	0.66	1.8	11.09
	270	0.51	1.5	12.02

values along with pore volume and diameter. The emergence of surface area during thermal treatment is likely related to the reduction of organic compound and volatilization, which results in the formation of matrix in char Cantrell et al. (2012). The surface area of biomass was $1.37 \text{ m}^2/\text{g}$ which rose to $2.09 \text{ m}^2/\text{g}$ at 250°C with 52% increase in HTC process, while in torrefaction there was a decrease and the values of surface area was below zero as compare to biomass. There are 3 categories of pores depending upon their internal diameter, named as micropores (less than 2 nm), mesopores (From 2 nm to 50 nm), and macropores

(larger than 50 nm) Rouquerol et al. (1999). Pore diameters of all the samples are given in Table 2, which clearly indicate that all are mesopores in nature. The pore size were mesopores as classified by International Union of Pure and Applied Chemistry (IUPAC). The pores on char hold the moisture content and increase the water holding capacity of soil Theis and Rilling (2009). The values of pore diameter and pore volume of HTC char were greater than torrefaction char. The highest pore volume for HTC process was observed at 200°C of 7.08×10^{-3} with 388% of increase in pore volume, while the pore volume for torrefaction pro-

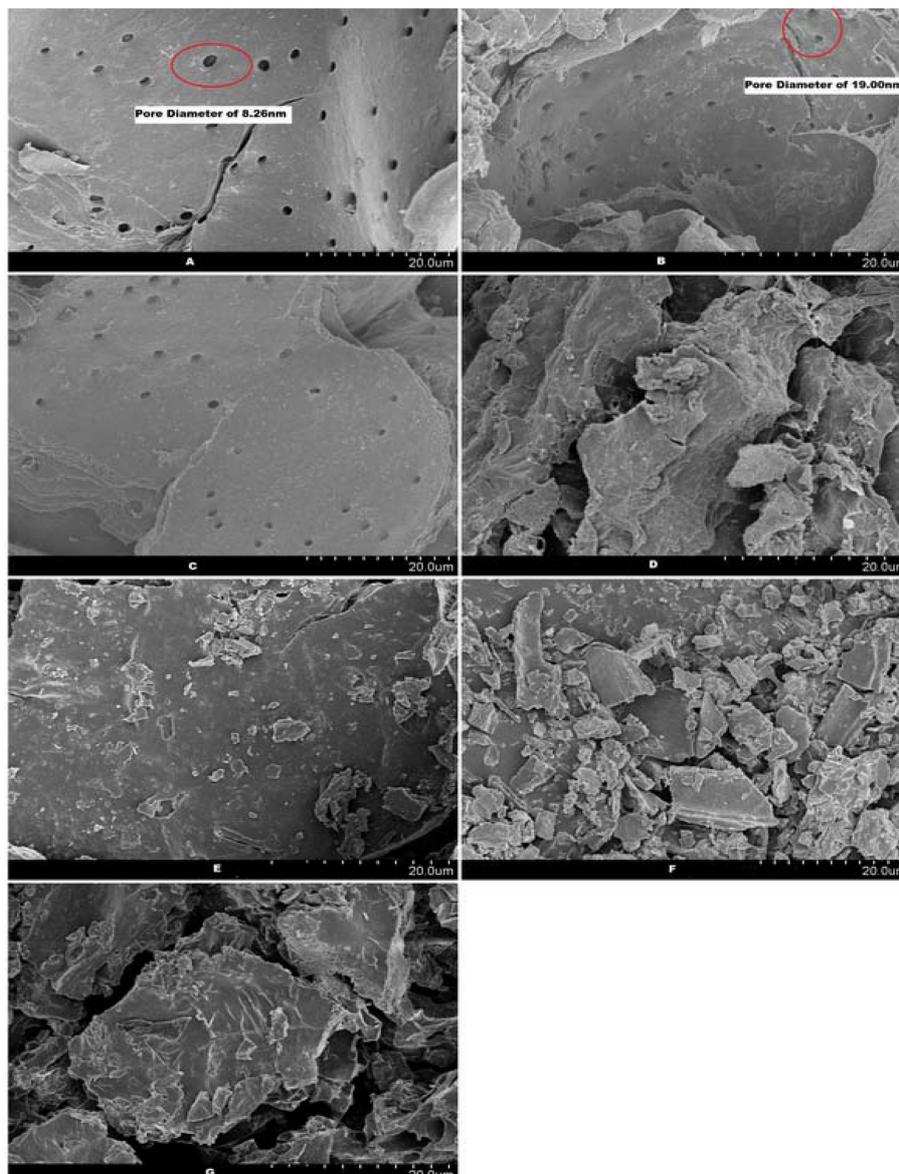


Fig. 1. Scanning Electron Microscope (SEM) images of Hydrochar. (A) Sample, (B) HTC 200°C , (C) HTC 230°C , (D) HTC 250°C , (E) DRY 250°C , (F) DRY 260°C , (G) DRY 270°C .

Table 3. Elementary Analysis of HTC and dry torrefaction

Pretreatment	Temperature (°C)	N (%)	C (%)	S (%)	H (%)	O (%)
Biomass		0.32	41.35	ND	4.86	53.47
Hydrothermal Carbonization (HTC)	200	0.60	41.70	ND	4.76	53.10
	230	0.45	42.25	ND	4.96	51.71
	250	0.47	43.22	ND	4.68	49.12
Torrefaction	250	0.57	41.84	ND	6.04	52.22
	260	0.64	43.21	ND	5.96	51.45
	270	0.59	45.96	ND	5.77	49.84

Table 4. Energy content, energy densification ration and energy yield of HTC and dry torrefaction

Pretreatment	Temperature (°C)	Mass Yield (%)	Energy Content (MJ/kg)	Energy Densification Ratio	Energy Yield (%)
Biomass		100	16.42		
Hydrothermal Carbonization (HTC)	200	70.98	16.81	1.15	81.62
	230	63.43	18.10	1.24	75.65
	250	57.39	18.29	1.25	71.74
Torrefaction	250	69.20	22.01	1.30	89.96
	260	65.5	21.28	1.26	82.53
	270	59.8	19.74	1.17	69.96

cess was below 1.8×10^{-3} . The pore volume started to decrease as heated above 200°C in HTC process. (Zhang and Changfu, 2013) reported that polar (*Populus davidiana*) showed 300% increase pore volume that biomass in an electric furnace at 450°C for 40 minutes. The pore volume started to decrease as heated above 200°C in HTC process. The biomass was having the pore diameter of 8.26 nm, the pore diameter of HTC char was also the highest of 19 nm at 200°C with 130% of increase while on the other hand torrefaction char pore diameter was a bit lower and highest of 12.02 nm was notice at 270°C with 45% of increase in pore diameter as shown in Fig. 1.

Table 3, shows the elementary analysis of HTC and torrefaction thermal treatment. Thermal carbonization results in the diminution of oxygen and enhancement of carbon. Loss of oxygen is responsible for the increase in energy content of char Hoekman et al. (2011). Carbon content started to increase as the temperature was raised. In HTC process at 250°C 43.22% of carbon content was noted with 4.5% of increase which is small amount, whereas in torrefaction process at 270°C 45.96% of carbon was calculated with 11% increase as compare to biomass. Oxygen content showed decrease as temperature was raised in both the pro-

cess. The value of hydrogen content in HTC process fell down however there was rise in the value of hydrogen in torrefaction process. Nitrogen was in very small quantity, whereas the sulfur was not detected.

The energy content, energy densification ratio along with energy yield is given in Table 4. Increase in temperature is directly proportional to increase in the energy content of char. For example Hoekman et al measured energy content of woody biomass by HTC process and found out that there was about 39% of increase in energy content after carbonization at 255°C. Yan et al found out 36% of increase in energy value of lobby pine. While Inoue et al reported 11-73% increase when treating Konara (Oak) at 250-350°C. Torrefaction process showed the higher value of energy content along with energy yield. The energy content of biomass was calculated as 16.42 MJ/Kg. There was about 11.3% of increase in energy content when heated until 250°C in HTC process while there was approximately 34.04% of increase in energy content when carbonized at 250°C in torrefaction process. Yen at al reported that torrefaction process produces high energy dense char than HTC process. Hydrochar has an energy density equivalent to different types of coals (e.g., brown, lignite, etc.) Berge et al.

(2011). The energy content of lignite and brown coal ranges from 10-20 MJ/kg. The energy content of torrefaction char at 250°C was highest of 22.01 MJ/kg which resemble to lignite coal. The energy content start to decline when heated beyond 250°C. The energy densification ratio and energy yield of torrefaction process was also higher than HTC process. The highest energy densification ratio of 1.30 and energy yield of 89.96 % was seen at 250°C in torrefaction process.

4. Conclusion

HTC and torrefaction are propitious methods to convert lignocellulose biomass to high dense solid fuel for subsequent thermochemical conversion. In both processes temperature significantly affects the product distribution and character of solid product. In HTC process mass yield was greater than torrefaction process. However the energy content of torrefaction char was much higher than HTC char. Biomass has increased carbon content indicating that the biomass has been transformed into a fuel with resembling to coal. Torrefaction char showed similar energy content with lignite coal. The energy densification ratio and energy yield was also higher in torrefaction process than HTC process. The pore volume and pore diameter values of HTC process were higher than torrefaction. So HTC char can be favorable to hold moisture and increase water holding capacity when char is applied in soil as compare to torrefaction process. Thus, it can be concluded that dead leaves can also be converted to low rank coal with torrefaction process.

This study analyzes on the initial scoping experiments; there is no attempt to optimize the conditions of torrefaction in particular reaction kinetics. To demonstrate techno economic feasibility mass and energy balance of both HTC and torrefaction and subsequent thermal conversion process (gasification or fast pyrolysis) must be scrutinize as well.

Acknowledgements

This project was supported by Korea Ministry of Environment (MOE) as “The Eco-Innovation 21 project (2013 000150004)”.

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