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Hydrothermal Carbonization and Hydrothermal Liquefaction of Water Hyacinth

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Abstract- *Hydrothermal conversion of biomass are becoming very attractive to the researchers as it produces biochar, namely hydrochar (HTC) and biocrude (HTL) comparatively at low temperature. Water hyacinth is a locally available biomass that has potential as a renewable energy source for biofuel production. In this article, water hyacinth was hydrothermally treated at 260, 280 and 300℃. The solid and liquid products were characterized by means of ultimate analysis, proximate analysis, scanning electron microscopy (SEM), x-ray diffraction (XRD), thermogravimetric analysis (TGA), differential thermal gravimetric analysis (DTG) and higher heating values. The highest values of higher heating value were found the HTC and HTL obtained at 300˚C was obtained for water hyacinth 27.3 MJ/kg and 22.98 MJ/kg. Carbon content of the HTC and HTL products was greater than the raw biomasses. XRD profiles show amorphous carbon only for hydrochar of water hyacinth.*

Keywords: water hyacinth, hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL), reactor, hydrochar, bio-oil, calorific value.

1. INTRODUCTION

Consumption of energy is rapidly increasing day by day because of an increase in population and thus the demand of alternative energy sources has been steadily increasing. Excessive use of fossil fuels and rapid urbanization are the cause of increasing CO_2 in the atmosphere at an alarming rate, which result various adverse environmental effects like climate change due to global warming. In addition, sulfur oxides (SO_x) is released due to fossil fuel combustion that cause acid rain. Thus, it is become a challenge of every country of the world to be a country with low air pollution [1]. As a source of clean and renewable energy, biomass is becoming important to energy agencies all over the world. Biomass is the fourth largest energy sources in the world. However, it has also inferior physical and chemical properties such as low calorific value, hydrophilic nature, low bulk density, high alkali content in ash, poor grind ability results into highly inefficient combustion and handling properties of biomass [2]. Biomass can be converted into biofuel or biogas that can be used as fuel or can be burned directly. The amount of carbon emitted by the biomass is equal to the total amount of carbon absorbed during its growth. So that it is carbon neutral, and it is a renewable form of energy [3]. Water hyacinth is cellulosic biomass which contains the organic components like lipid, protein and nitrogen materials [4]. Water hyacinth contains 48% hemicellulose, 20% cellulose and 3.5% lignin. Water hyacinth can produce biofuels and various value-added products as it contains a high amount of cellulose and hemicellulose. The productivity of water hyacinth is very high and thus it can be used as feedstock material for the production of biofuel [5]. The main disadvantage of water hyacinth it clogs reservoir, channel and river course as it produces roots [4].

Hydrothermal process is one of the most prominent, effective process among all the thermochemical processes to convert water hyacinth into high carbon content products in absence of oxygen [6]. Hydrothermal process is the physical and chemical transformation of the biomasses at high pressure (5-40 MPa) and high temperature (200-600℃) water [7]. This process converts the biomasses into three different highly carbonaceous products as solid, liquid and gas by hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL) and hydrothermal gasification (HTG) respectively [8, 9]. This paper presents hydrothermal carbonization (HTC) and hydrothermal liquefaction (HTL) processes of water hyacinth which produces high carbon content coal-like and oil-like products respectively at temperatures in the range of 250-355℃ [11, 12] and in autogenic pressure. Hydrothermal carbonization is the dehydration, decarboxylation and thermochemical process for the conversion of solid biomasses into high carbonaceous product at elevated temperature (180-250℃) and pressure (2-10MPOa) for achieving higher calorific value by achieving its carbon content [13]. The solid products obtained from HTC process is called hydrochar [14]. There are a lot of applications of biochar like water purification, CO_2 sequestration, fuel cell catalysis, bio-imaging, gas

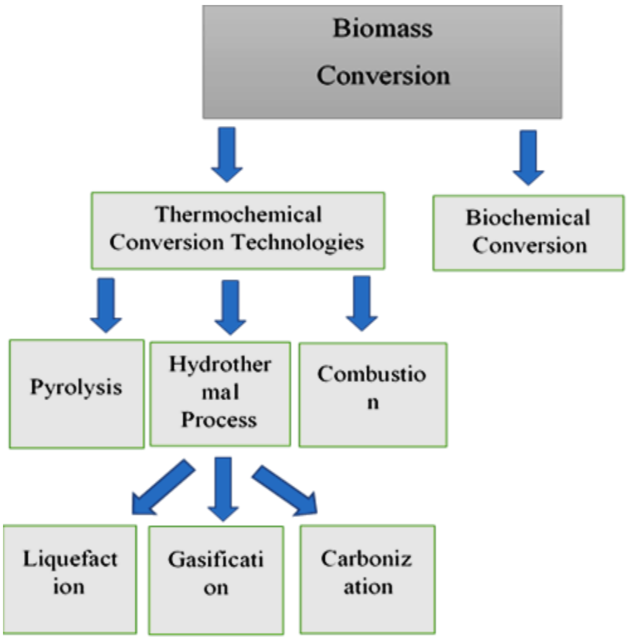

Fig.1: Biomass conversion technologies [10]

sensors, energy storage, and drug delivery [11]. On the other hand, hydrothermal liquefaction is the thermochemical conversion of biomasses into a liquid product as bio-oil in presence of water at the temperature of 300–350 °C and a pressure of 5–20 MPa for 5–60 min [15, 16]. This process can easily liquefy any kind of material like agriculture residue, sewage sludge, municipal waste, forest residue, manure, etc. During the HTC and HTL processes, various reactions like hydrolysis, dehydration, decarboxylation, condensation polymerization, and aromatization take pace while converting biomass [17]. HTC and HTL processes are very costly processes as the reactor is very expensive; however, the processes have been performed in a much cheaper cost compared to other works as the reactor was custom made using locally available materials. The char produced from HTC process can be used as coal for the generation of electric power and the bio-oil produced from HTL can be mixed with other fuels for using as an alternative fuel. Temperature, size of a biomass particle, rate of biomass heating, type of solvent media, pressure, pH value and residence time are great factors in these processes to have a higher carbon content. Among all the thermochemical processes, HTC and HTL were chosen since these processes take less time at comparatively lower temperature [18, 19]. Also, it may be used for synthesizing of biomass at aqueous phase at relatively low cost [20]. Most importantly, materials with high moisture content of 90% or more can be used since pre-drying is not necessary as water is used as the solvent, which yield higher carbon content and higher calorific value [21]. Hydrochar was characterized by means of ultimate analysis, proximate analysis, scanning electron microscopy (SEM), x-ray diffraction (XRD), thermogravimetric analysis (TGA), differential thermal gravimetric analysis (DTG), mass yield, energy yield, energy density and higher heating values. And bio-oil was characterized by means of ultimate analysis, proximate analysis, thermogravimetric analysis (TGA), differential thermal gravimetric analysis (DTG), mass yield, energy yield, energy density and higher heating values. The feed materials were characterized to find its suitability for HTC and HTL processes and to compare the result of processed hydrochar and bio-oil with the raw sample.

2. MATERIALS AND METHODOLOGY

2.1 Materials

2.1.1 Water Hyacinth

Water hyacinth was collected from a pond in Chuadanga, Bangladesh. It was crushed and cut into small particles.

Fig.2: Dried Water Hyacinth

2.1.2 Reactor

The material selected for the reactor was stainless steel (grade 304). The designation stainless steel covers a wide range of alloys with different properties. One property common to all stainless steels is that they contain at least 12% chromium. The diameter and the thickness of the reactor is 71.12 mm and 2.8 mm respectively.

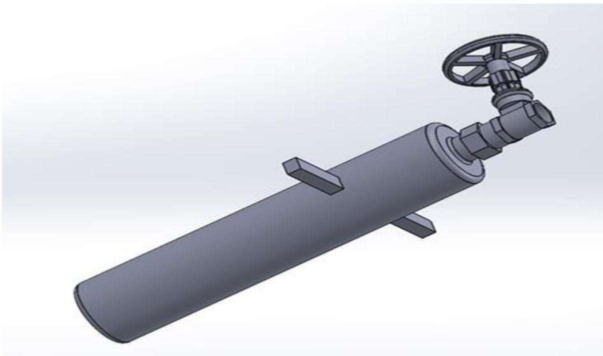

Fig.3: Reactor designed in SOLIDWORKS

Fig.4: Reactor

2.2 Experimental Procedure

At first water hyacinth was collected from the pond and washed to remove all the impurities and then dried at 110˚C temperature for about 3-6 hours for measuring the moisture content. After that, it was cut with a micro hammer cutter mill to use it for the process. The experiments were performed with RH and deionized water in a batch 900 ml Parr reactor. Approximately 25 grams (dry basis) of micro-algae and 250 ml of deionized water were added to the reactor to carry out the process. The mass ratio of 1:10 for all the biomasses was used to ensure enough water was added to the reactor to fully submerge the solid biomass. The mixture was stirred for about 3 minutes; the reactor was sealed. The reactor was then heated to the desired reaction temperature using a muffle heating furnace and the HTC and HTL reactions were carried out for the desired residence time maintaining the biomass water mixture to within ±5°C of the reaction temperature. The reaction temperature was 300°C and single residence time 2 hours was kept to carry out the experiment. After that, the reactor was submerged in cold water until the temperature reached the atmospheric temperature. Then, the reactor valve was opened and the gaseous product was released. The remaining solid-liquid mixture was passed through a filter to separate the hydrochar from the liquid product. The hydrochar and hydro oil was then dried and kept separately for further analysis. The hydrochar and bio-oil were also analyzed for ash content and ultimate analysis. The reactor pressure was not controlled in the experiment and was kept autogenic with the vapor pressure of water at the corresponding temperature.

Fig.5: Experimental Setup

Fig.6: HTC Product of Water Hyacinth at 300℃

3. RESULTS AND DISCUSSION

3.1 Bulk Density for Water Hyacinth

Bulk density is the volumetric density which is defined as the mass of many particles of the material divided by the total volume they occupy. The total volume includes particle volume, inter-particle void volume, and internal pore volume. The bulk density of water hyacinth was 24 (gm/cc).

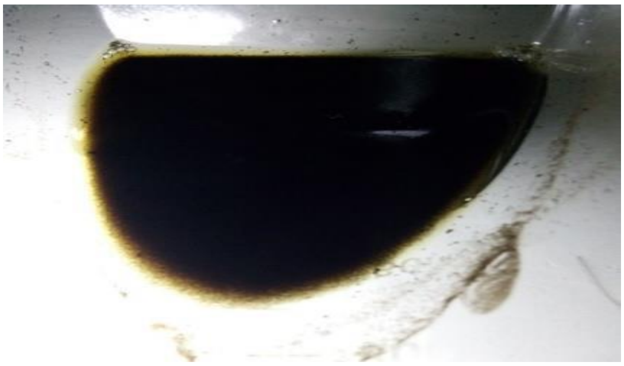

Fig.7: HTL Product of Water Hyacinth at 300℃

3.2 Moisture Content of Water Hyacinth

For measuring moisture content, the water hyacinth was dried in an oven for at 105℃ for 2 hours. The change in weight was then expressed as the percentage of moisture absorbed denoted by the following equation-

$$MC = \frac{M_f - M_{dry}}{M_{dry}} * 100$$

Where,

$MC = Moisture\ content\ of\ the\ sample$

$M_f = Final\ mass\ of\ the\ sample$

$M_{dry} = Mass\ of\ the\ dried\ sample$

Finally, the moisture content of water hyacinth was 8.58%.

3.3 Higher Heating Value

The energy contained in a food or fuel is the higher heating value which is determined by measuring the heat produced by the complete combustion of a specified quantity of it and a primary parameter in design the process of thermochemical conversion apparatus of biomass. This higher heating value is known as higher calorific value (HCV) which is measured by the "Bomb Calorimeter" apparatus expressed in in joules per kilogram.

Table 1: Higher heating value of raw, HTC and HTL products

Material	HHV (MJ/kg)
Raw	16.10
HTC-300℃	27.30
HTL-300℃	22.98

3.4 Mass Yield, Energy Yield and Energy Density of HTC and HTL Products at 300℃ Temperature

$$\text{Mass Yield} = \frac{\text{Mass of dried pretreated solid}}{\text{Mass of dried feedstock}} \times 100$$

$$\text{Energy Densification Ratio} = \frac{\text{HHV of pretreted sample}}{\text{HHV of raw feedstock}}$$

Energy Yield = Mass Yield × Energy Densification Ratio

The mass yield of water hyacinth was 54.2%.

Table 2: Energy Yield, energy density of raw, HTC and HTL products

Material	Energy Yield (wt %)	Energy Density
HTC-300℃	93.30	1.70
HTL-300℃	77.36	1.42

3.5 Proximate and Ultimate Analysis

Proximate analysis was done for measuring volatile material fixed carbon and ash content of the products. And ultimate analysis was done to know the percentage of carbon, hydrogen, nitrogen, oxygen and sulfur in the products of water hyacinth.

Table 3: Proximate and ultimate analysis of water hyacinth

	Proximate analysis			Ultimate analysis				
	VM (%)	FC (%)	Ash (%)	C (%)	H (%)	N (%)	O (%)	S (%)
Raw	60.1	23.3	19.6	46.78	6.95	0.47	45.65	0.15
HTC-300	44.10	39.79	16.11	60.20	8.50	0.54	30.51	0.25
HTL-300	60.21	39.79	--	53.20	10.50	.54	35.51	0.25

3.6 X-ray Diffraction Analysis (XRD)

X-ray diffraction (XRD) is a versatile non-destructive analytical technique for identification and quantitative determination of various crystalline phases of powder or solid samples of any compound and also provides the information about unit cell dimensions. A PHILIPS X Pert PRO X-ray diffraction system was used to get X-ray data for the samples at the Materials Science Division, Atomic Energy Center, Dhaka, which is a sophisticated X-ray diffractometer. The powder diffraction technique was used with a primary beam power of 40 kV and 30mA for Cu radiation. Crystalline carbon structure contributes that the peak strength indicates the amorphous carbon doesn't exists. From the curves there don't exists any amorphous carbon in the raw biomass and the HTC product that means that the raw biomass and HTC product of Water Hyacinth is amorphous.

3.7 Scanning Electron Microscopy (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the surface topography and composition of the sample.
The signals that derive from electron sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties.

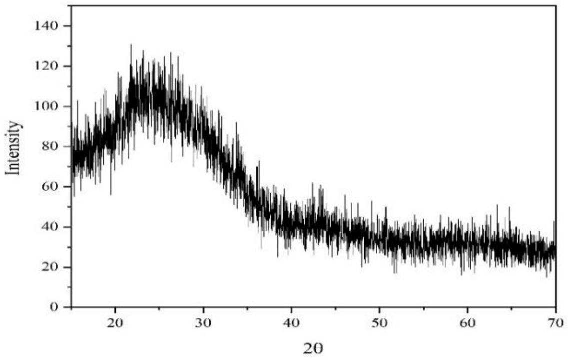

Fig.8: XRD profile of raw water hyacinth

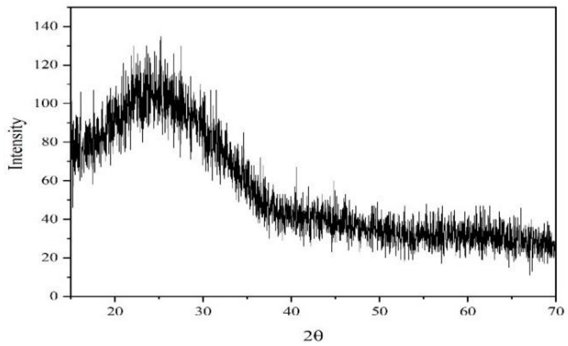

Fig.9: XRD profile of HTC water hyacinth

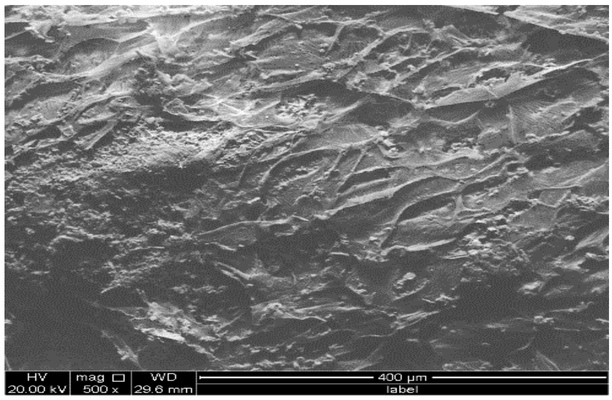

Fig.10: SEM profile of raw water hyacinth

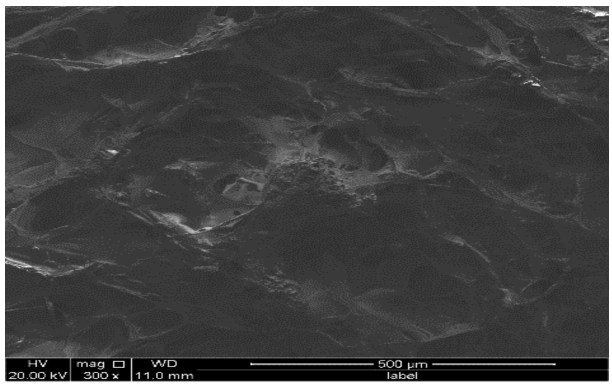

Fig.11: SEM profile of HTC water hyacinth

Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDS), crystalline structure, and crystal orientations (using EBSD). The microstructure measurement of the samples was done by using a Scanning Electron Microscope (SEM), Model No. S-3400 N, Hitachi installed at Atomic Energy Centre, Dhaka, Bangladesh. As it can be seen in Figures 10 and 11 that the surface of hydrochar are porous whereas the raw biochar does not have any trace of porosity on the surface. The hydrothermal process takes away some hydrocarbon from the biomass, thusly produces the pores on the surface.

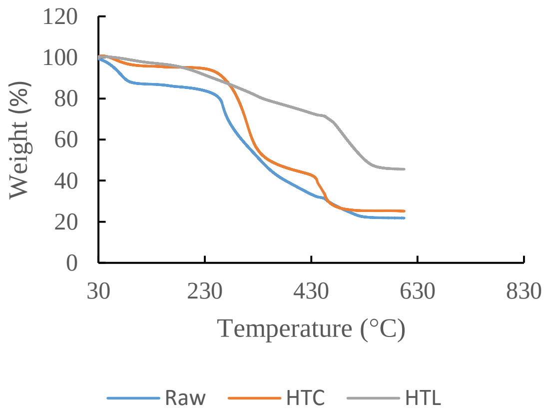

Fig.12: TGA profile of water hyacinth

3.8 Thermogravimetric Analysis (TGA) and Differential Thermal Gravimetric Analysis (DTG)

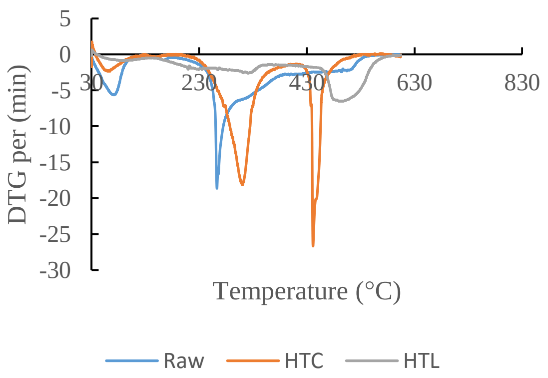

Fig.13: DTG profile of water hyacinth

TGA is a method of thermal analysis in which mass of a sample is subjected as a function of temperature. TG diagram provides information about thermal stability of substances, initial and intermediate products and solid residue composition. DTG is the derivative form of TG which provides information regarding the rate of change of mass with respect to time. The height of DTG curve at any temperature indicates the highest rate of change of mass. A PerkinElmer TGA 8000 analyzer was used to get TGA data for the samples at the Materials Science Division, Rajshahi University, Rajshahi, which is a sophisticated TGA analyzer.

Figure 12 represents the TG analysis curve for raw, carbonized and liquefied water hyacinth and the Figure 13 represents the corresponding DTG curve for the same. The weight loss of raw, carbonized and liquefied products is about similar up to the temperature 270°C. At the first stage weight loss was slow because of loss of low weighted volatile substances. The major loss of mass of raw starts at 270°C and continued up to about 480°C. The major loss of bio char starts at 270°C and ends at 440°C and again starts at 450°C and continued up to 480°C. The loss of mass is very gradual for bio-oil from 270°C to 450°C and rapid loss is from 450°C to 510°C. After that every curve follows a constant path which ensures the ash percentage after combustion. So, the second stage of combustion represents the combustion stage in case of treated sample which starts at 270°C to 480°C for hydrochar and 270°C to 510°C for bio-oil. At every stage the TG curve of treated product was at the upper position from raw product. Besides the ash percentage after combustion is also higher than raw due to the treatment process.

5. CONCLUSIONS

Hydrothermal carbonization and liquefaction can produce a wide variety of products like homogenized solid, coal-like fuel and oil from biomasses like water hyacinth. These processes are great technologies for waste management as well. It was found that reaction time, reaction temperature, pressure, and the particle size were the most important parameters for controlling the HTC and HTL processes as they had a great effect on hydrochar solid yield, ash content, O/C-ratio, carbon content, energy densification and energy yield. The highest values of higher heating value were found the HTC and HTL obtained at 300˚C was obtained for water hyacinth 27.3 MJ/kg and 22.98 MJ/kg. SEM image showed the degradation of raw biomass yielded porous hydrochar. The XRD profiles shoed the presence of amorphous carbons which is produced at low temperature conversion process at around 22°. TGA profile showed the absence of moisture at low temperature in treated samples compared to the raw biomass. The reactor was fabricated with a locally available materials and simple in construction compared to others available reactor all around the world. The reactor can be modified by attaching several accessories like a pressure gauge, pressure release valve, temperature sensor, etc. Though this product needs further treatment like esterification, the carbon content was better than other research works those have used water as a medium. As the demand of alternative energy sources have been steadily increasing with nonrenewable sources in day by day, the conversion of water hyacinth by HTC and HTL processes is worth closer attention.

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