Production and Characterization of Hydrochar and Biocrude of Yard Waste from Tectona Grandis using Hydrothermal Carbonization

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Abstract

Research on the study of tectona grandis for adsorption of dyes, extraction of chemicals dissolved in it for pharma industries is studied from many years. Few researchers have explored the use of tectona grandis in thermo-chemical process such as torrefaction, and pyrolysis. But the study to use of hydrothermal carbonization (HTC) to convert leaf litter to value added products of tectona grandis for varying process conditions is not performed. This research is focused to ascertain the role of HTC process parameters on hydrochar and biocrude produced from tectona grandis leaf litter. HTC experiments were conducted in a batch reactor. Various process parameters such as temperature and residence time which affects the yield of hydrochar is reported. HTC of yard waste is carried out at 210ºC for a residence time of 20 min in a batch reactor which gives the hydrochar yield of 65% with higher heating value of 26.63 MJ/kg. Characterization of hydrochar performed with proximate analysis, ultimate analysis, SEM and FTIR showed that hydrochar properties are better compared to feedstock properties which can be effectively used as solid fuel. The liquid biocrude separated from solid hydrochar is analyzed using UV spectroscopy. It is found to contain the compounds such as 5-HMF, dibenzofuran, naphthalene and anthracene.

Keywords: *Hydrochar, FTIR, SEM, HTC*

1.0 Introduction

Renewable energy production and their applications in India is taking a fast growth thereby reducing the consumptions of fossil fuels and pursue India in low carbon development path (MNRE 2020). The exploration of renewable energy sources like solar and wind energy has increased rapidly in India due to various schemes initiated by government of India. Biomass energy potential in India from agriculture, agro residual waste and municipal solid waste (MSW) is estimated at 18000 MW and more research has to be focused in this area. India generates 62 million tonnes of municipal solid waste (MSW) every year and only 12 million tonnes of waste is treated and the remaining amount of waste is dumped in open sites

(Malico et al. 2019). The large portion of the MSW collected in India is organic waste (food and yard waste) which will vary between 54 and 64% (Sharma, Sarmah, and Dubey 2020). There is a need to treat this waste instead of open dumping which will generate methane gas and leads to carcinogenic effect on ecosystem and environment.

Yard waste in gardens and commercial farms are routinely burnt or composted due to seasonal availability and lack of storage. The demand for teak timber (tectona grandis) due to its superior properties, versatility and the variety of applications is well documented. The demand for teak has led to the increased plantations in tropical and subtropical countries. The global teak plantations are estimated to be three million hectare with major share in India (44%) followed

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by Indonesia (33%) (Palanisamy, Hegde, and Yi 2009) (Tewari, Álvarez-González, and García 2014). Teak plantations in countries in Africa and Central America are aimed to satisfy the global demand for durable timber. The plantations of tectona grandis is managed both in large scale government owned establishments and small locally owned private forest land owners (Pachas et al. 2019). The life span of teak tree can be as high as 200 years, which makes it a candidate for carbon sequestration (Sreejesh KK et al. 2012). Allelopathy of teak tree promotes monoculture with plantations. The litter produced in teak plantations are exceedingly teak litter. The extract from litter is reported to be used in a variety of applications including removal of malachite green (Oyelude, Awudza, and Twumasi 2018). Due to the antimicrobial properties of teak leaf litter, the natural degradation of teak leaves is time consuming. The teak litter production per hectare is reported to be about 5020 kg of litter per hectare per year (Egunjobi 1974).

Biomass feedstocks can be broadly classified as lignocellulose and non-lignocellulosic types: biomass leaf residue from tectona grandis is lignocellulosic biomass (LCB). The LCB feedstocks are rich in cellulose, hemicellulose and lignin (Singhvi and Gokhale 2019) (Sharma and Dubey 2020). High moisture, fibrous nature, bulk volume and low energy content properties of LCB makes it unsuitable for energy conversion process (Sharma, Sarmah, and Dubey 2020). Utilization and efficient management of LCB waste is considered as an important technological achievements necessary in the world of increasing energy demand. LCB yard waste and waste from hardwood timber industry are some of the feedstocks have sparked research interest in recent years (Devadiga, Shetty, and Saidutta 2015). The seasonal leaf litter residue of tectona grandis plantation is currently composted naturally and is not an time efficient processing methods. Various thermo-chemical methods such as gasification, pyrolysis etc. is explored by researchers to derive energy and other end product applications from LCB.

Nowadays research interest in the treatment of biomass in the presence of water known as hydrothermal process. Hydrothermal process is a thermochemical process in which biomass is suspended in water from few min to hours in a reactor (Oliveira, Blöhse, and Ramke 2013). The temperature of biomass and water mixture can raise up to $600^{\circ}C$ inside the reactor and based on the working temperature it can be categorized as hydrothermal carbonization ($180\text{-}280^{\circ}C$), hydrothermal liquefaction ($280\text{-}400^{\circ}C$) and hydrothermal gasification ($400\text{-}600^{\circ}C$).

Hydrothermal carbonization (HTC) has gained more importance among the above-mentioned process due to low working temperature and cost-effective process. HTC mimic the formation of natural coalification process and the experiment was first conducted by Bergius in 1913 (Sevilla, Maciá-Agulló, and Fuertes 2011) (Ramke et al. 2009). This

coalification process was later reinvented and referred to in various names by researchers as hot compressed water treatment (Inoue, Hanaoka, and Minowa 2002), aqueous phase carbonization (Mochidzuki, Sato, and Sakoda 2005), subcritical water treatment (Wiboonsirikul and Adachi 2008), wet Torre- faction (He et al. 2018) and hydrothermal treatment. HTC is a thermochemical process in which biomass is converted into useful products at a temperature of ($180\text{-}250^{\circ}C$) under saturated pressure of (2-10 MPa). The main advantage of HTC over other thermochemical process is pre-drying of moisture content in biomass can be eliminated since the entire process occurs in water. The biomass is converted to useful products such as hydrochar solids with porous texture and structure along with biocrude liquid product (Oliveira, Blöhse, and Ramke 2013). HTC process is effectively used for the treatment of both LCB and non-LCB.

Various researchers conducted HTC for different lignocellulosic feedstocks such as coconut fiber (Liu et al. 2013), Miscanthus (Kambo and Dutta 2014), pine wood (Kang et al. 2012), corncob (Calucci, Rasse, and Forte 2013), wood sawdust (Wang et al. 2017), and bamboo (Yao and Ma 2018). But till date no research on hydrothermal carbonization of hydrochar and biocrude of tectona grandis leaf litter is reported. In this paper production and characterization of hydrochar from tectona grandis is performed using various techniques such as proximate analysis and ultimate analysis, SEM and FTIR. The biocrude obtained after separation of solid hydrochar from HTC of tectona grandis is analysed using UV spectroscopy to determine various chemicals dissolved in it for extraction is an important research gap which is not addressed so far in the field of HTC.

2.0 Materials and methods

2.1 Biomass feedstock

The teak leaf litter was collected from M.S. Ramaiah University of Applied Sciences campus gardens at Peenya, Bengaluru, a total of 1 kg of teak leaf litter is collected for the experiments. The leaves were dried in oven at $105^{\circ}C$ for 4 hours to remove all moisture. The dried leaves were pulverized to fine powder with a domestic blender and sieved in 100 mesh to produce biomass powder of approximate particle size of 150 microns. Each of the experiment includes addition of 10 gm of teak leaf litter powder with 100 gm of water to the reactor.

2.2 Experimental procedure

The teak leaves is heated to a temperature of $210^{\circ}C$ and it took one hour of time to achieve this temperature inside the reactor, after attaining this desired temperature the residence

time was started. The carbonization was conducted for a residence time of 20 minutes. The cooling of the HTC reactor is done under ambient conditions. The parted liquid sample (biocrude) separated from the slurry mixture is stored in an airtight container for further analysis. The solid sample (hydrochar) is dried in an oven at 80ºC conditions for 2 hours and stored in separate airtight container for analysis.

2.3 HTC Reactor

The HTC reactor is designed in-house with a volume of 330 mL and the heat is supplied to the reactor using a band heater with rated power of 250 W. The reactor temperature is measured with J type thermocouple. The heater is controlled with a temperature controller that monitors the reaction temperature using the thermocouple sensor. The reactor is also fitted with a pressure gauge that can measure pressure up to 70 bars. The reactor takes approximately 1 hour to reach 210ºC.

2.4 HTC Process parameters

Temperature: The process parameters for the experiments were selected based on the published values in literature (Wang et al. 2018). The selected temperature of 210ºC is based on the degradation of biomass constituent molecules. For example, hemicellulose degradation starts at 180ºC, cellulose degradation starts above 200ºC and lignin degradation temperature is between 200ºC and 500ºC. Lignin having high molecular cross linked polymer shows slower degradation than hemicellulose and cellulose. This can be attributed to the simpler molecular structure of hemicellulose and cellulose with minimal cross linking molecules compared to lignin molecules (Sharma, Panigrahi, and Dubey 2019). Teak wood is a tropical hardwood waste which consists of cellulose (40-45%), hemicellulose (24-40%) and lignin (18-25%) (Tarasov, Leitch, and Fatehi 2018). In our study the teak leaves was heated to 210ºC and the characteristics of feedstock and hydrochar is depicted in Table 2.The yield of hydrochar calculated using Eq. (1) as follows:

$$Yield\ (\%) = \frac{Weight\ of\ hydrochar}{Weight\ of\ feedstock(dry\ leaves)} \quad ...(1)$$

Residence time: Residence time is another important factor involved in the conversion of HTC process. It influences the quantity, composition of hydrochar and longer residence time increases the severity of the reaction (Pauline and Joseph

Table 1: Feedstock and HTC input to the experiment

Weight of feedstock	Biomass-water ratio	Particle size	Weight of hydrochar	Yield (%)
10 gm	1:10	150 microns	6.5 gm	65

2020). Longer duration of residence time decreases the solid yield of hydrochar and shorter residence time increases the yield of hydrochar (Wang et al. 2018).In our experimental set up the residence time is 20 min for constant reaction temperature of 210ºC. So both temperature and residence time can affect the HTC process and therefore both these parameters are defined using the term hydrothermal severity (Ro). Table 2 shows the hydrothermal/reaction severity of hydrochar. Hydrothermal severity (R_0) is based on Arrhenius eq. (2) given by:

$$R_0 = te^{\frac{(T-100)}{14.76}} \qquad ...(2)$$

Where, R_O= Hydrothermal severity, t isreaction time (min), T isreaction temperature (ºC)

Table 2: Hydrothermal severity of hydrochar

Temperature (ºC)	Time (Min)	SF
210ºC	20	5.02

Severity factor (SF) is defined as log (R_O) that signifies the various process parameters used in the HTC process. As the SF increases hydrochar yield decreases because at higher temperatures degradation of cellulose and hemicellulose occurs due to hydrolysis process. Therefore hydrothermal severity should be controlled during HTC process in order to use of hydro char for various applications and recovery of nutrients such as xylose and glucose from the liquid product (Wang et al. 2018). So hydrothermal severity has to be designed in order to create the hydrochar properties for varieties of applications. But there is a lack of research findings to develop the hydrochar properties for specific application using nature of feedstock, particle size of feedstock, solid load of biomass, biomass to water ratio and pH solution. So specific characteristics of hydrochar can be developed based on these variables in order to improve process efficiency and large scale commercialization of HTC technology in industries.

3.0 Results and discussions

The properties of hydrochar is mainly studied with characterization of hydrochar as discussed below:

3.1 Proximate analysis and Ultimate analysis

Proximate analysis is used to determine the energy content of hydrochar which shows the percentage of the ûxed carbon, volatiles, ash, and moisture content in the given sample. The amounts of ûxed carbon contribute to the heating value of

coal and high volatile matter content indicates the ignition capacity of fuel. The proximate analysis of hydrochar is shown in Table 3:

Table 3: Proximate analysis of Feedstock and hydrochar

Sample	Fixed Carbon (%)	Vola. Matter (%)	Ash (%)	HHV (MJ/Kg)
Feed-stock	10.4	84.3	5.30	21.96
Hydro-char	20.2	75.2	4.6	26.63

From the proximate analysis it can be observed that volatile matter content of hydrochar is decreased compared to raw feedstock which indicates decreased pollution emission when combusted. So this characteristic of hydrochar is very useful when it is co-combusted with coal because coal having high volatile ratio and biomass with low volatile ratio leads to separate combustion regions in co-firing and increased efficiency in combustion (N. Zhang et al. 2020). The decrease in volatile matter and increase in carbon content in the hydrochar is mainly due to polymerization and condensation reactions occurred during HTC process. Ash content of hydrochar is relatively lower with respect to raw feedstock ash content due to dissolved inorganic compounds of raw feedstock in liquid phase after carbonization process. Therefore lower the ash content less environmental ash related problems of hydrochar. Higher heating value (HHV) of the sample is obtained using correlations from(Channiwala and Parikh 2002). HHV of the hydrochar is high compared to feedstock which can be used as solid fuel applications.

The ultimate analysis shown in Table 4 gives various elemental composition such as carbon, hydrogen, oxygen and nitrogen present in the sample.

Table 4: Ultimate analysis of feedstock and hydrochar

Temp (^{O}C)	C (%)	H (%)	N (%)	O (%)
Feed-stock	53.7	6.3	0.4	39.6
Hydro-char	65.4	5.8	0.4	28.4

Table 5 shows the ratio of elemental composition of hydrochar (H/C and O/C) atomic ratios. In accordance with the van-krevlin diagram, these ratios changes significantly from feedstock to hydrochar. The H/C and O/C ratios shows the reaction pathway of feedstock to effective solid fuel known as hydrochar. From Table 5 it is very clear that H/C and O/C ratios have decreased from feedstock to hydrochar due to dehydration and decarboxylation reactions which indicates carbonization process in the hydrochar.

Table 5: Ultimate analysis of feedstock and hydrochar

Temp (^{O}C)	H/C	O/C
Feed-stock	1.41	0.55
Hydro-char	1.06	0.33

3.2 SEM Analysis

The surface morphology, particle shape and pore size distribution of the hydrochar is obtained using scanning electron microscope (SEM). Figure 1 shows the hydrochar SEM images and it is very clear that hydrochar maintains an irregular pattern on its surface this is due to decomposition of lignocellulosic component of biomass which led to this rough surface on hydrochar. The hydrochar particles were found to be agglomerated ranging from 10 to 50 µm agglomerates this shows the destruction of biomass structure due to weakening of cell wall. Since HTC experiment is conducted for a short residence time and low temperature the porous structure formed on the hydrochar is very small because the degradation of lignin requires very high carbonization temperatures and residence time. So in order to increase the pore volume on the surface of hydrochar activation processes can be adopted. For applications such as soil amendment, supercapacitors and low cost adsorbent the pore volume of hydrochar should be very high. So overall the hydrochar has low pore size distribution and coarse size particles that can be easily blended with coal particles in co-firing applications.

3.3 FTIR (Fourier Transform Infrared spectroscopy)

Figure 2 shows the FTIR spectra of tectona grandis and the derived hydrochar. The spectra shown in red colour indicates the raw biomass (tectona grandis) and blue spectra indicates the hydrochar. Tectona grandis biomass shows very strong peak at 3066 cm^{-1} shows the presence of O–H groups, medium peak at 2603 cm^{-1} indicates aldehydes (H–C=O stretch), small peaks at 2850 cm^{-1} and 2217 cm^{-1} shows alkanes and nitriles group. 1141 cm^{-1} peak marks the stretching of C–O functional groups and finally the broad peak at 900 cm^{-1} gives alkenes (=C–H bend). So overall tectona grandis biomass structure consists of alkanes, alkenes, nitriles and alcohol functional groups. The intensity of peak which showed at 2217 cm^{-1} became very weak and shifted to 2297cm^{-1} showed that compound containing Ca™N (nitriles) is changed to different types of compound due to carbonization temperature. Broad peak between 1200 cm^{-1} and 800 cm^{-1} which contains C–O and (=C–H) groups has been disappeared indicating decarboxylation reaction of hydrothermal carbonization. Aldehyde C–H groups is also
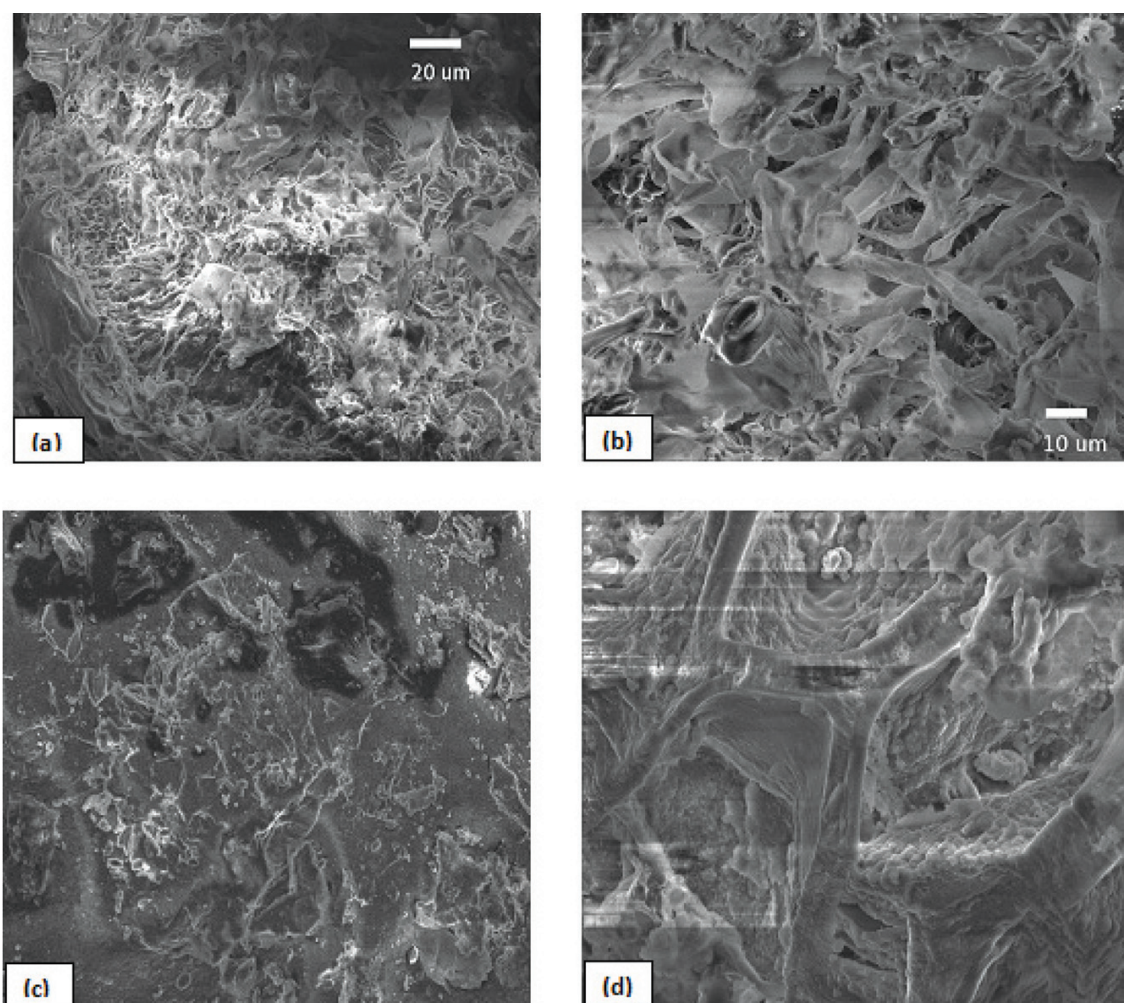
Figure 1: Surface morphology of Hydrochar for different resolution in SEM

stretched between 3000 cm^{-1} and 2800 cm^{-1}. So after conduction of HTC process the small peaks between 3500 cm^{-1} and 3000 cm^{-1} combined together to form a broad peak. This stretching vibration of –OH groups shows the possible formation of 5– HMF compound. So from these results it is confirmed that product obtained from tectona grandis has undergone various chemical reactions to undergo carbonization process.

3.4 UV Spectrometry

The biocrude seperated from solid hydrochar is analyzed using UV spectrometer. UV spectrometry is routinely used for quantitative assessment of concentration of a substance in a solution. Biocrude obtained from the HTC process typically contains compounds such as 5-hydroxymethylfurfural (5-HMF), furfural compounds, furan and their derivatives with visible peaks between 230 and 280 nm are detected with UV spectroscopy. The compounds reported from these methods are produced by carbonization of cellulose present in the cell wall as reported in (Nomura, Minami, and Kawamoto 2020). The spectral characteristics of 5-HMF using UV spectroscopy yields absorption maximum at 284 nm and peaks at 229 – 230 nm range for molar absorption coefficient (Hudz, Leontiev, and Wieczorek 2019) (Adu et al. 2019) and (J. Zhang et al. 2013). The presence of absorption of wavelength longer than 300 nm shows the presence of conjugated double bond systems such as naphthalene and anthracene(Nomura, Minami, and Kawamoto 2020). Additionally the presence of carbon oxygen double bonds, carbon nitrogen double bonds can be seen due to the presence of peaks in the range of 200 to 320 nm range. Further fractionation and distillation can be done on biocrude to segregate the compounds.
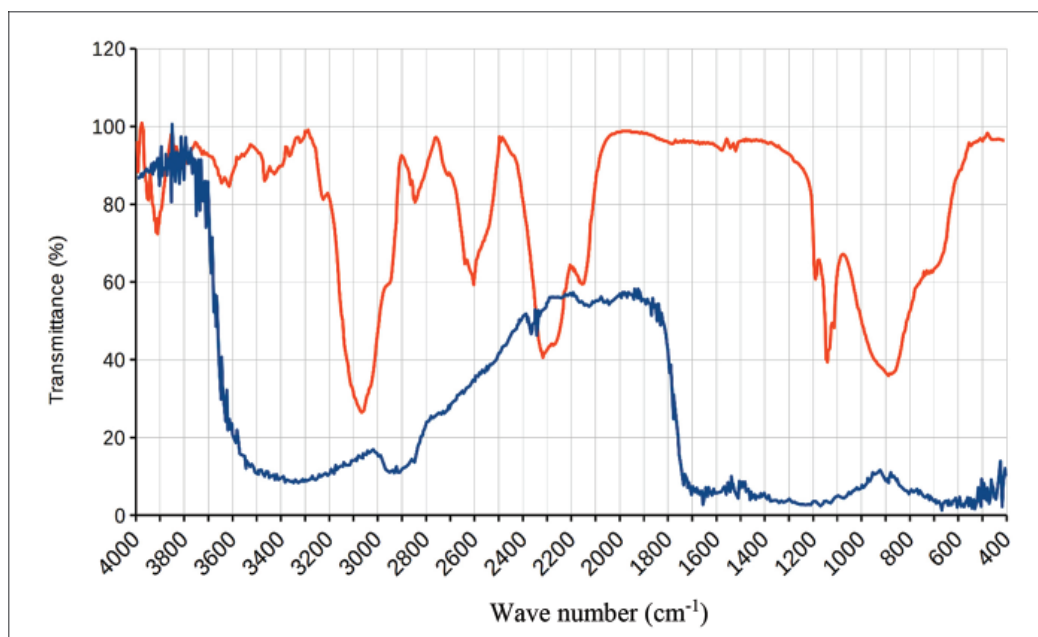
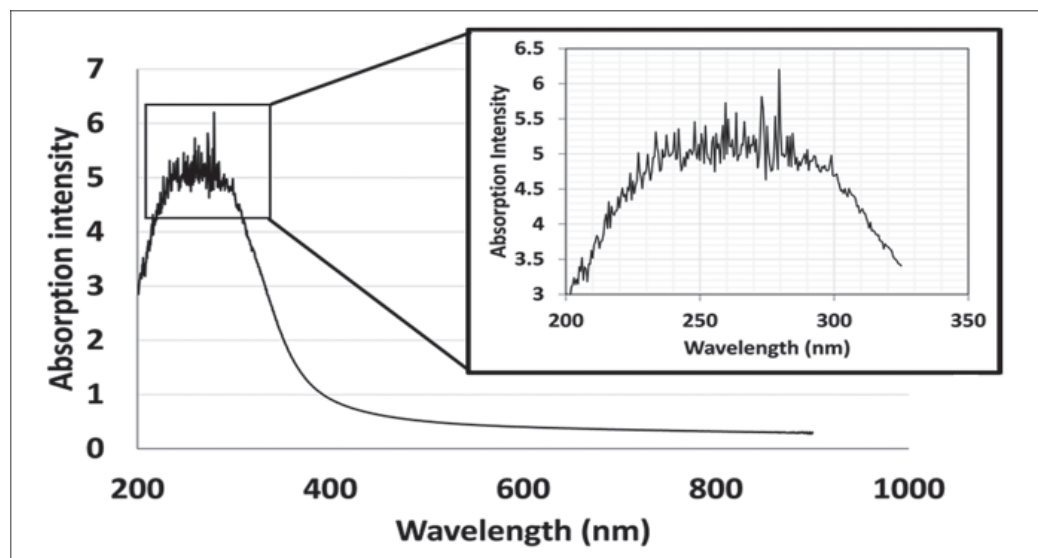**Figure 2:** FTIR Spectra of Tactona grandis and derived Hydrochar

Figure 3: UV absorption of biocrude from the HTC process

4.0 Conclusions

Process parameters and characterization of hydrochar obtained from yard waste of tectona grandis is analyzed. Process temperature and residence time used to conduct HTC of yard waste is 210ºC and 20 min. Since tectona grandis is LCB which contains high percentage of carbon content and low moisture content (dry biomass) the residence time used for our experiment is quite low compared to non LCB such as food waste, municipal solid waste, sewage sludge where the

residence time is usually high (in hours). The following were the observations made during the study.

- The yield of hydrochar obtained is 65%, as a small portion of tectona grandis is lost during separation of solid hydrochar from biocrude and the remaining portion of the feedstock is converted to gaseous products.
- Proximate analysis of hydrochar shows that volatile matter of initial feedstock in tectona grandis is reduced from 84.3% to 75.2% and fixed carbon increased from 10.4 % to 20.2%. This property of hydrochar with decreased volatile

matter and increased carbon content will increase the efficiency of combustion when it is co-combusted with coal since the coal has high volatile ratio and biomass with low volatile ratio leads to separate combustion regions in co-firing.

- Ultimate analysis of hydrochar shows that H/C and O/C atomic ratios are reduced due to dehydration and decarboxylation reactions which indicates the degree of carbonization in the hydrochar.
- SEM analysis, presented the hydrochar particles to have the size of 10 to 50 μm agglomerates due to various chemical reactions undergone by biomass which weakens the cell wall of biomass. The pore size distribution of hydrochar is very low due to short amount of residence time.
- FTIR analysis of tectona grandis indicated the presence of alkanes, alkenes, nitriles and alcohol functional groups in the hydrochar and stretching of these functional groups at various wavelengths confirms carbonization process has occurred in the raw biomass. The long stretching of –OH groups shows the formation of 5-HMF which is an intermediate by-product of HTC process along with various liquids dissolved in the biocrude of HTC liquid product.
- UV spectrometry of bio crude indicated peaks below 300 nm that corresponds to compounds such as 5-HMF, dibenzofuran, furan, and naphthalene.

In future work, effect of particle size, biomass to water ratio, pH, catalytic role in the yield of hydrochar and its properties can be investigated along with the activation techniques to improve the pore volume of hydrochar. It is also found that the biocrude is a complex mixture of dissolved organic compounds, phenolic substances, sugars and furfural derivatives; extraction of these compounds is very beneficial for pharma and food industries and thus a detailed study on the analysis of liquid products of HTC can be carried out in future work.

5.0 References

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