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Effects of Hydrothermal Temperature and Time of Hydrochar from Cattail leaves

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Abstract. Hydrochar have been successfully synthesized from Cattail leaves via hydrothermal carbonization. This research study the effect of hydrothermal temperature (160-200 °C) and reaction time (4-24 h) to develop porosity and surface area. The sample have been characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy were employed to characterize morphology, surface function and disorder in carbon structure respectively. The results revealed that hydrothermal-carbonization process affect on the properties of hydrochar. The hydrothermal temperatures and time were increased resulted in the decomposition of hydrochar gradually increased amorphous carbon and aromatic groups on surface of hydrochar. Cattail leaves was hydrothermal carbonization at 200 °C for 12 h resulted in the most degradation of hemicellulose and cellulose.

Keywords: Hydrothermal Carbonization, Cattail leave, Biomass.

INTRODUCTION

Renewable energy development in Thailand has increased to replace the dependence on coal, natural gas and petroleum due to rising domestic consumption and declining production. Therefore, renewable energy from biomass is an important to reduce the import of fuels and the emission of greenhouse gases. The similarity of biomass characteristics with fossil fuels make it unique to be used for power, heat, and fuel generation. Thailand is an agricultural country, there are many residues from agriculture such as rice straw, coconut shell, palm shell and weed. We are interested in using biomass and waste for significant environmental benefits, energy security and long-term sustainability [1-2]. Biomass refers to biological matter or waste obtained from living organisms that has solar energy stored in it. It is deemed to be a potential energy source and is considered to be inexpensive, clean, and environmental friendly. Biomass is a lignocellulose material composed of hemicellulose, cellulose, and lignin are considered to be an abundant and renewable resource which can be converted into solid, liquid, and gaseous form using biochemical, physicochemical, and thermochemical technologies [3].

Hydrothermal processing is a thermochemical process that involves thermal disintegration of biomass in hot compressed water, wherein a series of complex reactions causes changes in the water's physical properties [4]. The biomass-to-carbon conversion can proceed under relatively mild conditions (less than 300°C) [5]. During HTC, the carbohydrate components from biomass are broken up and dissolved in the water, following a complex cascade of aldol-reactions, cycloadditions and condensations, a carbon rich solid product is obtained. The remaining liquid phase contains some unreacted sugars and/or oligomers that can be used for a variety of practical purposes such as for example the production of bioplastics and biofuels [6]. The HTC process is very attractive due to its simplicity, low-cost and energy and CO₂ efficiency, it can also be classified as "Non toxic" since it does not involve organic solvents, catalysts or surfactants. Hydrothermal process is energetically favourable when compared to traditional

pyrolysis, because it uses milder conditions, does not need previous drying of the precursor and is exothermic. Moreover, HTC processes avoid gas emissions and the formation of tars, which are unavoidable during pyrolysis. Finally, the advantages of HTC in comparison with other carbonization treatments due to the high efficiency of the process since most of the carbon stays bounded to the carbonaceous material [7-8]. The main product of choice is a solid product known as hydrochar thus, the process selected is hydrothermal carbonization. The hydrothermal carbonization process produces a higher yield of hydrochar with higher energy efficiency, higher porosity, higher level of carbon recovery, and lower ash content [9-11]. Hydrochar have attracted continuous attention due to their wide current and potential applications. They possess a variety of fascinating properties such as superior chemical, thermal stability, high surface areas, and tunable structures, by which they can be extended to the fields of adsorption, sensing, catalysis, energy storage and conversion, separation science, etc [12-13].

In this research, There is interesting to use Cattail leave as a raw material for the production of hydrochar because it is a carbon source. Cattail leave is one of the most common weeds in Thailand. It can be found worldwide in wetlands, fens, margins of ponds and lakes, roadside ditches, irrigation canals, and backwater areas of rivers and streams [14]. Cattail uses solar energy to grow rapidly and can breed in large numbers. It has an impact on the environment and waste water. Cattail leave is a biomass composed of 38.5% cellulose, hemicellulose, 37.6% lignin, 12.8% ash, 11.1% [15]. Objective of this research, to investigate the morphology, functional group on the surface and disorder in carbon structure of Cattail leave were reacted by hydrothermal carbonization. The parameters for carbon preparation, including hydrothermal temperature and time, are investigated and discussed in terms of the change of composition and morphology of carbon.

EXPERIMENT

- **Raw material**

Cattail leaves (CL) has derived from Ladkrabang, Bangkok, Thailand. Structure consists of hemicellulose, (37.6%) lignin, (12.8%) and ash, (11.1%). Previous to HTC process, cattail leaves was dried in oven at 80°C to remove moisture and consecutively weighted until no further weight loss and crushed using a blender to obtain a powder. these precursors were ground and sieved. The particle size of 1 mm was used to produce the hydrochars by the HTC process.

- **Preparation of hydrochar**

The hydrothermal process (HTC) of the precursors was carried out in a 50 ml. stainless steel autoclave using a volume of 60 ml. of deionized water and 30 g of biomass. The mixture was sealed into a Teflon vessel and then inserted in the autoclave, The reaction occurs in the range of 160-200 °C and 4-24 hr. (Table 1. shows the labels and reaction conditions) After hydrothermal treatment, the product was dried at 80°C for overnight.

TABLE 1. Conditions of cattail leaves derived hydrochar

Sample	Temperature (°C)	Time (h.)
CL160-4	160	4
CL160-8		8
CL160-12		12
CL160-24		24
CL180-4	180	4
CL180-8		8
CL180-12		12
CL180-24		24
CL200-4	200	4
CL200-8		8
CL200-12		12
CL200-24		24

- **Characterization**

Yield (%) of hydrochar was calculated as the applied formula.

$$Y(\%) = \frac{m}{m_0} \times 100$$

Where Y is the yield (%) of produced biochar, m is mass of produced hydrochar (g), and m₀ is raw cattail leave biomass (g). Fourier Transform Infrared spectroscopy was used to determine the function group on surface of sample by infrared radiation source. The FTIR spectra of the samples were recorded between 4000 and 400 cm⁻¹ in a Perkin Elmer Spectrum Two by ATR mode. The dried samples were brought to analyze the surface morphology by Scanning Electron Microscope (SEM, Zeiss EVO MA10). The specimens for SEM observation were prepared by depositing the powder sample onto specimen-stubs with conductive double sticky carbon tapes, and then sputter-coating the sample surface with Au to prevent electrical charging during examination. Imaging was done in the high vacuum mode under an accelerating voltage of 10 kV, using secondary electrons. The structural was measure by using Raman spectroscopy (DXR SmartRaman). The source of radiation was a laser operating at a wavelength of 532 nm.

RESULTS AND DISCUSSION

- **Yield of Hydrochar**

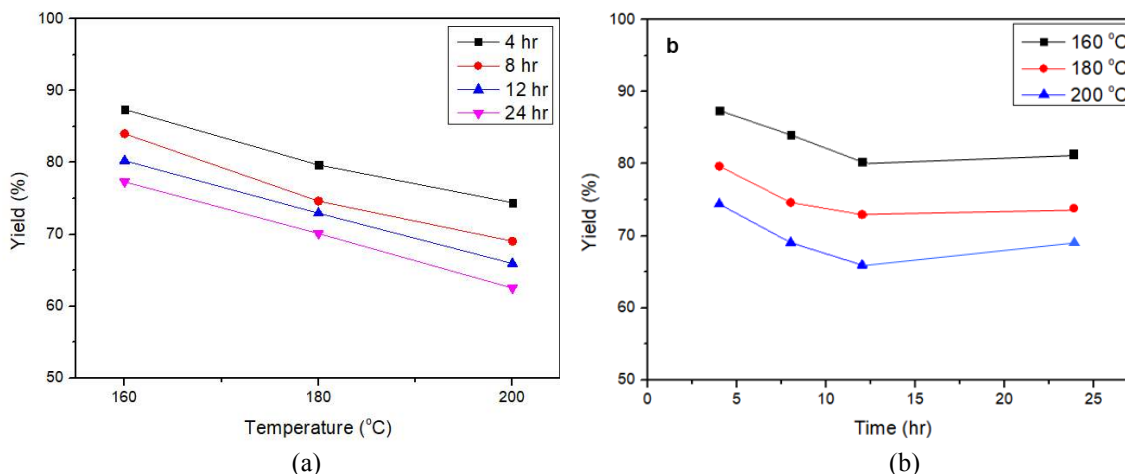


FIGURE 1. Yield (%) of hydrochar products through hydrothermal process at (a) different temperatures (b) different times

Fig. 1a and b shows yield (%) of hydrochar products through hydrothermal process at different temperatures and times. Hydrochar presents the main solid product of the process. The increase of reaction temperature leads to a significant decrease of solid yield due to moisture content in the structure was eliminated and the decomposition of the hemicellulose component and some of the cellulose and lignin. Increasing the temperature from 160 °C to 200 °C reduced the yield on average by 30%. The yield of hydrochar significantly decreases with temperature. Biomass loses more mass at 200 °C than at 160 °C and 180 °C. The higher temperature causes a relatively increase of solid mass loss, which can be due to the greater effect of water in the hydrolysis reaction [16-17]. The temperature of 200 °C seems to show the least of yield. When the reaction time is longer than 12 hours, the yield increases. Within the investigated parameters, longer residence times resulted in yield of hydrochar increase due to re-polymerization reaction of decomposition biopolymer. The biopolymer are reformed into carbon, which reduces the surface area of hydrochar. The reaction time provided the decomposition of biomass less than the temperature.

- External Surfaces of Resulting Carbon Using SEM

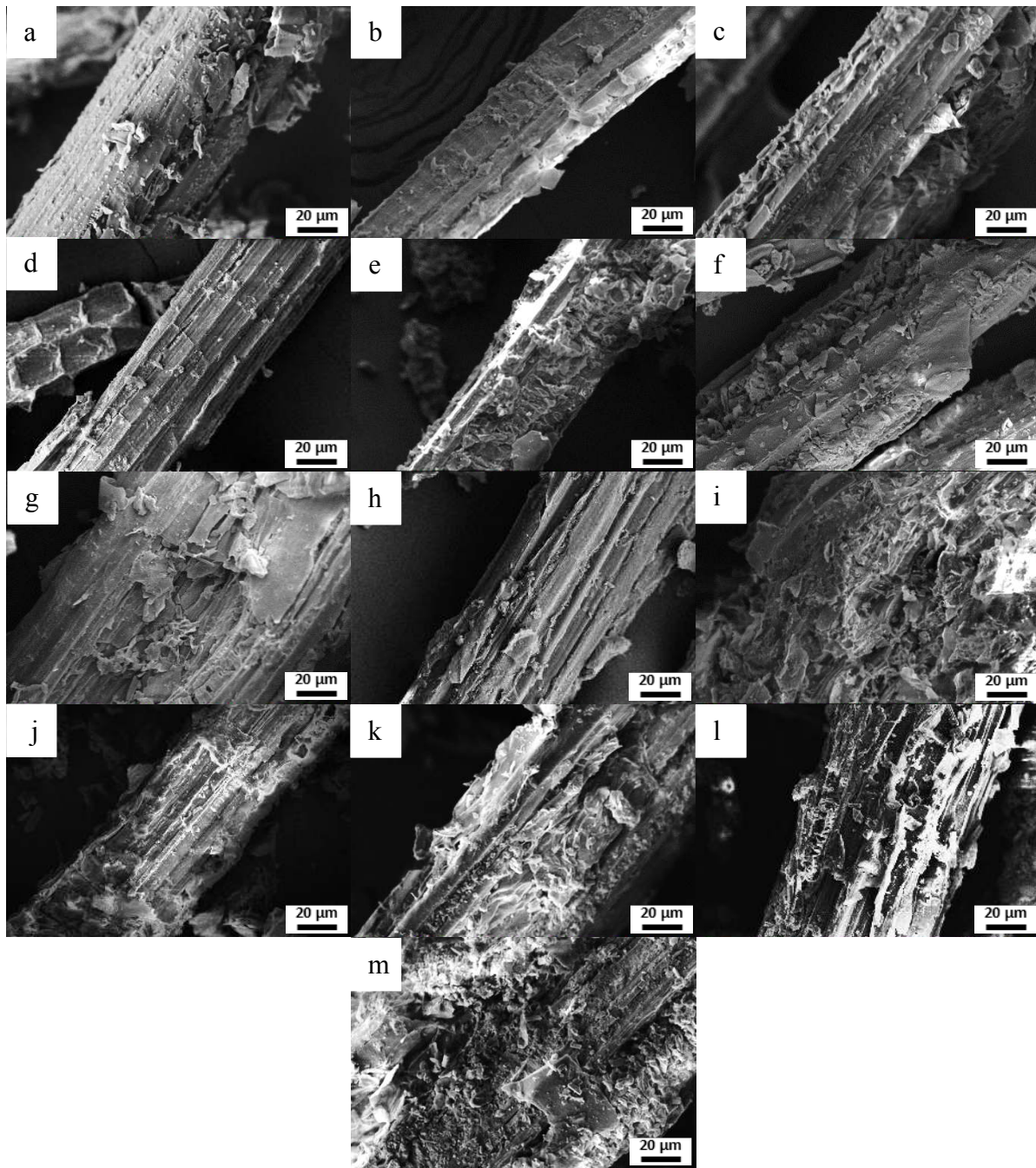


FIGURE 2. SEM images (500x) of Cattail leaves through hydrothermal process at (a) Cattail leaves, (b) CL160-4, (c) CL160-8, (d) CL160-12, (e) CL160-24, (f) CL180-4, (g) CL180-8, (h) CL180-12, (i) CL180-24, (j) CL200-4, (k) CL200-8, (l) CL200-12 and (m) CL200-24

Scanning electron micrographs of the surface morphology of the feedstock and different reaction temperatures (160, 180, and 200°C) for 12 h are given in Fig. 2(a-d). After hydrothermal treatment significant changes on the surface morphology can be found at different temperature. When increase temperatures provide polymer bond are more break compared to the feedstock. At temperature of 200°C showed that the hemicellulose were destroyed

significantly because water molecules can diffuse through the structure dramatically. This structure implies that the formation pathway of hydrochar may be attributed to hemicellulose hydrolysis followed by polymerization reaction since both stage temperatures are less than 230°C. Therefore, at temperatures below 230°C, most of the decomposition is hemicellulose, followed by cellulose and lignin, respectively. Temperature has a significant affect on the fracture structure over reaction time. At temperature 200 °C for 12 h is optimum condition for surface improvement of hydrochar which result in increased surface area and porosity.

- **Functional Group of the Raw Materials and Hydrochar**

TABLE 2. Conditions of cattail leaves derived hydrochar

Wavenumber (cm ⁻¹)	Functional group	Description
3680-3000	O-H stretching	Hydroxyl or carboxyl groups, alcohols from cellulose or phenols from lignin
3000-2800	C-H stretching	Aliphatic
1700	C=O stretching	Carbonyl, ester or carboxyl from cellulose and lignin
1600 and 1512	C=C stretching	Aromatic skeletal present in lignin
1380-1240	C-O stretching	Vibrations in lignin
1290-950	C-O stretching	Hemicellulose esters
1420	C-H bending	C-H deformation in lignin and carbohydrates
1060	C-O stretching	Vibrations in cellulose and hemicelluloses
860–724	C-H bend	Aromatic

The FTIR patterns of feedstock and hydrochar are shown in Fig. 2 and 3. The typical FTIR functional groups can be identified. The results are presented in Table 2 that spectra of feedstock mainly possess peaks at around 3680-3000 cm⁻¹ are assigned to O-H stretching from lignin, peaks around 3000-2800 cm⁻¹ represent the C-H stretching (Aliphatic). Peaks around 1700 cm⁻¹ are attributed to the stretching vibration of C=O of from cellulose and lignin. Peaks around 1600 and 1512 cm⁻¹ are stretching, representing aromatic which are found in the lignin [19]. Moreover, Peak around 1380-1240 cm⁻¹ are C-O stretching of lignin. Peaks around 1290-950 cm⁻¹ are attributed to the stretching stretching of C-O from Hemicellulose esters. The peaks located at 1420 cm⁻¹, which can be related to C-H deformation in lignin and carbohydrates. The absorbance peak of C-H bend at 860–724 cm⁻¹ indicates the presence of aromatic.

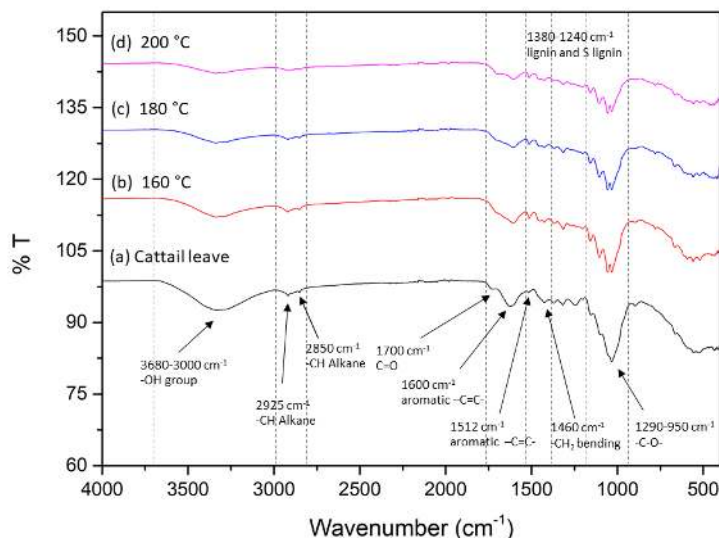


FIGURE 3. FTIR spectra of hydrochar for 12 hr at (a) Cattail leave (b) CL160-12, (c) CL180-12 and (d) CL200-12

Fig. 3. shows FTIR spectra of hydrochar products through hydrothermal process at different temperatures. Compared with the spectrum of feedstock, some differences appear after HTC treatment at 180°C. The absorption of

feedstock at 1700 and 1290-950 cm^{-1} disappeared at 180°C due to the majority of the hemicellulose is decomposed [20]. However, other peaks show similarity to feedstock. When the reaction temperature increases to 200°C, the cellulose peaks at around 1060 cm^{-1} (C-O stretching vibration) disappear, indicating that the cellulose is slightly decomposed. The reduction of the oxygen functions group corresponds to the O content. In addition, with temperature rising, the bands at 1600 and 1512 (C=C stretching vibrations) and 1700 cm^{-1} (C=O stretching vibrations) become wider and stronger obviously, and the absorbance peak corresponding to aromatic C-H appears at 860–724 cm^{-1} . These changes suggest that the aromatic rings are formed and/or recombined at higher temperature. In contrast, the broad absorption band corresponding to O-H vibrations at 3680-3000 cm^{-1} decreased with increasing temperature of the reaction, It can be confirmed that the dehydration reaction occurs. While, the bands 3680-3000 cm^{-1} and 1700 cm^{-1} represent O-H stretching and C=O stretching groups. It also shows that the hydrochar are divided from cattail leaves, forming oxygen-containing functional groups. The peaks at 1380-1240 cm^{-1} indicate that C-O groups decrease, meaning that lignin begins to decompose. The hemicellulose is significantly degraded at 200°C but cellulose decompose at 230°C and lignin begins to decompose at about 260°C due to its highly stable structure. Therefore, hydrothermal temperature at 200°C is optimum condition for improving the oxygen function group of hydrochar.

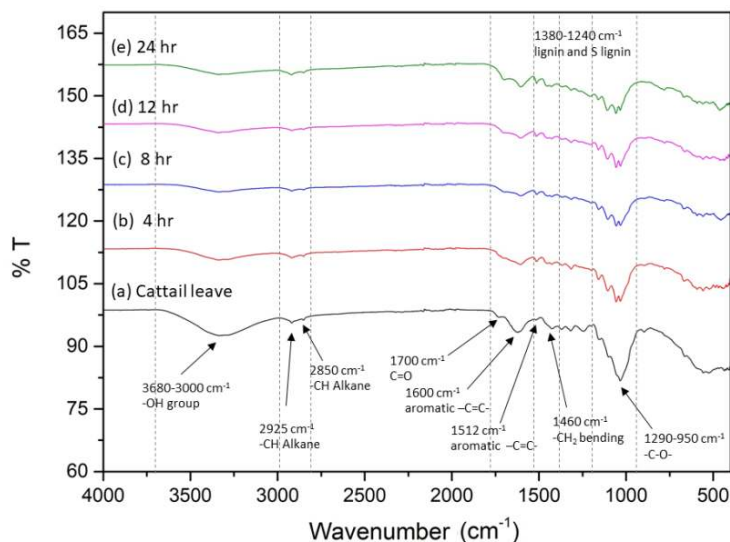


FIGURE 4. FTIR spectra of hydrochar at 200°C for (a) Cattail leave, (b) CL200-4, (c) CL200-8, (d) CL200-12 and (e) CL200-24

Fig. 4. shows FTIR results, as the reaction time increased, the peaks of the aromatic functional groups became stronger, and the C-O groups showed weaker signals. The changes of the relative peak intensities of hydrochar suggested that cattail leaves underwent dehydration, decarboxylation and condensation polymerization during hydrothermal carbonization. It can be indicated that decomposition of hemicellulose, cellulose and some lignin increase when hydrothermal for a longer time. Meanwhile, the aromatization might occur.

- **Structural Analysis of Hydrochar**

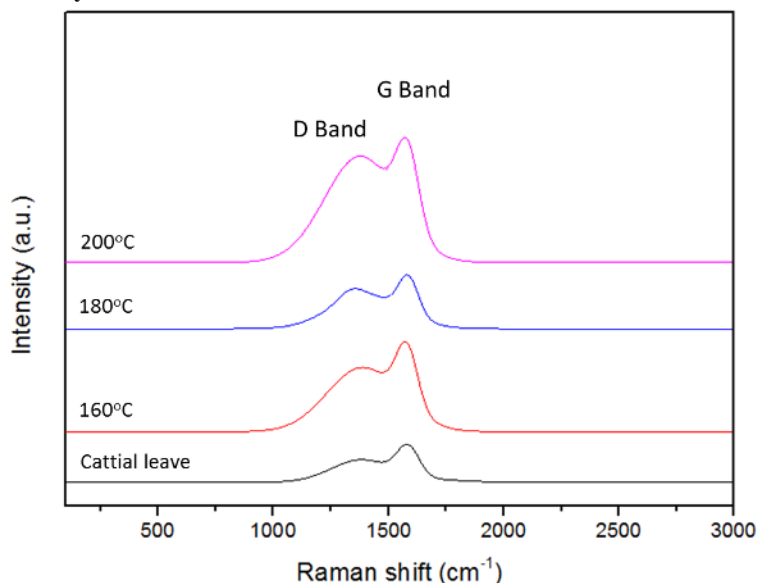


FIGURE 5. Raman spectra of Cattail leaves through hydrothermal process at 200°C for 12 hr and difference co-solvent treatment (A) CL, (B) CL-160°C, (C) CL-180°C and (D) CL-200°C

Fig. 5 shows raman spectra of hydrochars. Two strong peaks above 1380 and 1570 cm^{-1} can be seen as G band and D band respectively. The peak at 1570 cm^{-1} is attributed to an E_{2g} mode of graphite and is related to the vibration of sp^2 -bonded carbon atoms in a 2D hexagonal lattice, such as in a graphite layer. The peak at 1380 cm^{-1} corresponds to vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite [21]. Table 3 shows the I_D/I_G values for CL, CL-160°C, CL-180°C and CL-200°C were calculated to be 0.59, 0.70, 0.75 and 0.85 respectively. This high intensity ratio (I_D/I_G) indicate that there are more carbon defects. The hydrothermal temperature at 200 °C provide the most amorphous structure.

TABLE 3. Raman spectra information on hydrochar samples

Sample	I_D	I_G	cm^{-1} (D band)	cm^{-1} (G band)	I_D/I_G
CL	48.11	80.28	1383.35	1581.47	0.59
CL160-12	136.98	193.67	1352.30	1577.81	0.70
CL180-12	86.69	115.66	1390.65	1569.60	0.75
CL200-12	233.58	273.39	1375.13	1569.60	0.85

CONCLUSION

Cattail leave was converted to hydrochar by hydrothermal carbonization at 200oC for 12 hr in this work. The temperature are mainly affected the solid yield, the chemical and structural properties of hydrochar. With the increasing of reaction temperature the hydrochar yield decreased above 30%. The hydrochar derived from decomposition of hemicellulose, residual of cellulose and formation of amorphous carbonaceous compounds during HTC. While, The cellulose and lignin are thermally stable components. It decomposes when hydrothermal at higher temperatures. The influence of thermal decomposition process parameters improved product characteristics and provided the HTC process a promising technology for enhancing biomass fuel properties.

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