Carbohydrate Polymers 90 (2012) 102–108

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Wood chemistry and density: An analog for response to the change of carbon sequestration in mangroves

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ARTICLE INFO

Article history:
Received 21 February 2012
Received in revised form 2 April 2012
Accepted 1 May 2012
Available online 8 May 2012

Keyword:
Carbon sequestration
Cellulose
Lignin
Wood chemistry
Mangrove
FTIR

ABSTRACT

This study aimed to resolve the variations of physical and chemical properties of wood records measured in different mangroves with their annual carbon sequestration. The methods of investigation used were to examine growth rate by monitoring breast height diameter, wood chemistry and density, FTIR spectroscopy and thermogravimetry. Carbon sequestration rate showing an increase with density varied between 0.088 and 0.171 $\mu g\,C\,kg^{-1}\,AGB\,s^{-1}$, and *Avicennia marina* showed the maximum value and *Bruguiera gymnorrhiza*, the minimum. The changes in FTIR bands at 4000–2500 cm^{-1} and 1700–800 cm^{-1} were correlated to the variations in cellulose in mangrove woods and lignin to cellulose ratio ranged between 0.21 and 1.75. Thermal analyses of mangrove wood suggested that the fuel value index (985–3922) exhibited an increase with the decrease in maximum decomposition temperature and density. The seasonal variation of temperature and CO_2 were likely to affect chemical properties through changes in wood density.

1. Introduction

Recent studies indicate that the chemical and physical properties of the wood can be related to tree growth altered by elevated temperature and CO_2 (Kilpelainen et al., 2003). Although tropical forests play an active role in the global carbon cycle and climate, their carbon sequestration in terms of ligno-cellulose polymer, wood density and growth history remain poorly characterized compared to other ecosystems on the planet (Poussart, Mynemi, & Lanzirotti, 2006). The mangrove forest accounts for about 0.7% of tropical forest (Giri et al., 2011) and the region dominated by *Avicennia* can assimilate CO_2 by photosynthesis at higher rate than many other mangrove species (Alongi, 2009). The wood density can serve as proxy for growth in response to ambient CO_2 (Telewski & Strain, 1994; Telewski, Swanson, Strain, 1999). Again climatic change in terms of elevated CO_2 and temperature can affect chemical properties of wood, such as lignin content (Fengel & Wagner, 1984; Fukazawa & Imagawa, 1981; Gindl, Grabner, & Wimmer, 2000). Concentration of cellulose could be related to the changes in wood density (Megraw, 1985; Shupe, Hse, Choong, & Groom, 1997) and growth rate could significantly affect wood chemistry (Kramer & Kozlowski, 1979). This study shows how seasonally resolved physical and chemical properties of wood records at different ambient temperature and carbon dioxide can serve as proxies for reconstructing carbon sequestration of different mangroves.

2. Materials and methods

The study site is located in Indian Sundarban mangrove forest (21°32′ and 22°40′ N; 88°05′ and 89°E) at the land-ocean boundary of the Gangetic delta and the Bay of Bengal. Eight types of mangrove trees – *Avicennia alba*, *Sonneratia apetala*, *Avicennia marina*, *Xylocarpus granatum*, *Aegialitis rotundifolia*, *Ceriops decandra*, *Bruguiera gymnorrhiza*, *Heriteira fomes* were considered in this study period (September 2010–August 2011) and the increase in diameter (dbh, diameter at breast height) during the study period was considered to carbon sequestration using allometric equations of above and below ground biomass (AGB, BGB with dbh and density, Ray et al., 2011). These mangrove trees are common to forest and 5 ± 2 years old which grow between 8 and 10 m in height.

Micrometeorological data (temperature, relative humidity, rainfall) were recorded by using computerized weather station (Model: Davis 7440) and incoming radiation was obtained from ARL data-base (http://www.arl.noaa.gov/ready.html). The atmospheric CO_2 was determined by gas chromatography (Ganguly, Dey, Mandal, De, & Jana, 2008; Mukhopadhyay et al., 2002).

2.1. Samples and density

Different wood species in triplicate were used for both physical and chemical study. Powdered wood samples (5 g) were

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http://dx.doi.org/10.1016/j.carbpol.2012.05.001

Table 1
Seasonal variation of micrometeorological parameters.

Seasons	Rainfall (mm)	Air temp (°C)	CO_2 (ppmv)	Humidity (%)	Solar radiation (W/m^2)	Pressure (mm)
Pre monsoon	145.5	29.7 ± 13.65	364.7 ± 5.56	74.9 ± 1.80	439.8 ± 17.56	758.0 ± 1.73
Monsoon	925.9	28.9 ± 15.04	366.7 ± 5.48	80.7 ± 2.10	432.9 ± 14.76	563.1 ± 1.97
Post monsoon	22.5	17.7 ± 4.95	369.7 ± 13.12	78.4 ± 3.32	436.7 ± 17.68	760.8 ± 2.34

sieved (200 μm) and were used for analysis. Density (ρ) of blocks (2 cm × 2 cm × 4 cm) cut from wood discs was determined dividing sample oven dry weight by the dry sample volume (Ray et al., 2011).

2.2. FTIR spectroscopy

FTIR spectra were recorded with a resolution of 4 cm^{-1} on solid samples (2 mg) in KBr pellets using L120-000A infra red spectrophotometer (Perkin-Elmer). DTGS detector was used. The concentration of standard cellulose (E.Mark) in the pellets were varied between 1 and 5 mg/100 mg KBr. Spectral ranges of 4000–2500 and 1700–800 cm^{-1} were used for multiple regression analysis with cellulose concentration (Nuopponen, Birch, Sykes, Lee, & Stewart, 2006) and contribution for cellulose was established. Cellulose concentration data obtained from FTIR were compared with analytical data.

2.3. Wet chemical analysis

The relative distribution of cellulose and lignin in wood dust was examined by spectrophotometric method (Yemm & Willis, 1954; Sluiter et al., 2010). In this method the samples were extracted in 72% of sulphuric acid at 60 °C in a water bath. Upon completion of hydrolysis, mixture was diluted (4% sulphuric acid) and heated in autoclave for ½ h at 120 °C. The mixture after filtration under vacuum was used for the measurement of absorbance at 320 nm for acid soluble lignin (ASL) and residue was used for the measurement of acid insoluble lignin (AIL). Carbon and nitrogen were examined using CHN Analyzer (2400 Series-11, Perkin Elmer). Total phosphorous was analyzed by spectrophotometric method after the oxidation of the sample using perdisulphate oxidation method. Total protein was calculated multiplying the evaluated nitrogen (N%) by 6.25 (AOAC, 1990).

2.4. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was carried out under constant nitrogen flow (90 ml/min) at a heating rate of 20 °C/min using a DSC-TGA thermobalance (SDT Q600 V8.2 Build 100). The heating scans were prepared on 4 mg of the sample in the temperature range of 25–800 °C. Calorific values and FVI (fuel value index) were calculated from the following relations, respectively (Demirbas, 1997; Mainoo and Ulzen-Appiah, 1996)

$$\mathrm{CV\,(MJ/kg)} = 0.312(\mathrm{FC}) + 0.1534(\mathrm{VM}),$$

$$\mathrm{FVI} = \frac{\text{calorific value (cal/g)} \times \text{sp. gravity (g/cc)} \times \%\text{lignin}}{\text{Moisture content (\%)}}$$

where FC = fixed carbon and VM = volatile matter in percentages.

Statistical analysis was done by MINITAB (version 13.1) statistical software package.

3. Results and discussion

Micrometeorological parameters (temperature, rainfall, solar radiation, humidity and pressure) fluctuate in response to the monsoonal cycle (Table 1). Annual movement of inter-tropical convergence zone in this part of the world produces significant changes in micrometeorological parameters throughout the study period because of different temperature and pressure in different seasons. Seasonal variation of temperature showed a minimum during post monsoon and 70–80% of annual rainfall occurred during the monsoon period. The CO_2 records exhibited distinct seasonal variations from a maximum of 369.7 ppmv in the post-monsoon period to a minimum 364.7 ppmv in the pre-monsoon period (Table 1).

3.1. Wood density variables

The most interesting patterns were found concerned differences in wood density among mangroves. Mean wood density of eight mangroves varied from 505 ± 85 to 700 ± 48 kg m^{-3} and mean maximum wood density was observed in *A. alba* (Fig. 1) which was 38.6% higher than the minimum value (505 kg m^{-3}) found in *B. gymnorrhiza*.

3.2. Chemical composition

The differences in density were related to the changes in chemical compositions of mangrove wood. Mangrove wood samples had a large variation in the cellulose content 62.5–20.51% of dry weight (DW) (Table 2). The amount of lignin for the mangrove varied from 11.1 to 46.94 of DW which is inconsistent with the range found for tropical hardwoods (19.1–30.7%, Nuopponen et al., 2006). Abundance of lignin was found lower than cellulose and their ratio varied from 0.23 to 0.21 in *A. alba* and *A. rotundifolia*. But in case of *H. fomes*, *X. granatum* and *S. apetala* lignin to cellulose ratio ranged between 1.40 and 1.75. The mangrove wood had a mean molar C, N, P ratio of 748:8:1, a consistent composition reported for mangrove litter (1300:33:1, Gordon et al., 1996). However, significant deviation (3370:33:1) from the mean molar composition was found in the case of *B. gymnorrhiza* wood in which considerable concentration of protein-N was found with minimum phosphorous concentration (0.03%. Table 2).

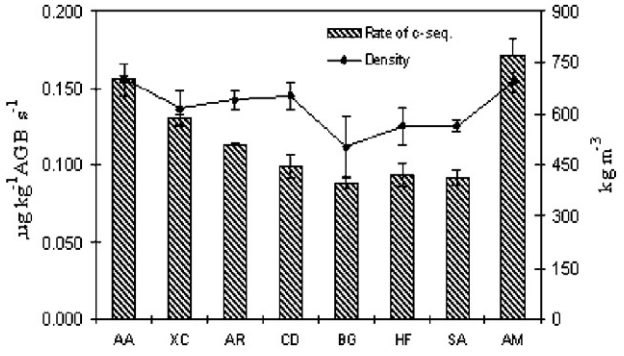

Fig. 1. During September 2010–August 2011, variation of carbon sequestration rates versus density among mangroves AA (*Avicennia alba*), XC (*Xylocarpus granatum*), AR (*Aegialitis rotundifolia*), CD (*Ceriops decandra*), BG (*Bruguiera gymnorrhiza*), HF (*Heriteira fomes*), SA (*Sonneratia apetala*), AM (*Avicennia marina*).

Table 2
Variation of mangrove wood density in kg m^{-3} (mean ± standard deviation) with cellulose versus lignin concentration (% of dry weight, DW) and other physicochemical parameters of eight different mangrove woods.

Samples	% Org C	% Total N	% Total P	% Moisture	Ash %	% Cellulose	%ASL	%AIL	Lignin/cellulose	% Protein	Density (kg m^{-3})
Avicennia alba	42.35 ± 1.26	0.284 ± 0.045	0.190 ± 0.005	36.7 ± 2.53	3.12 ± 1.00	48.25 ± 2.25	2.5 ± 0.25	8.6 ± 1.11	0.230	1.78 ± 0.08	700 ± 48
Avicennia marina	43.05 ± 1.86	0.731 ± 0.089	0.190 ± 0.004	43.9 ± 3.12	1.88 ± 0.55	29.39 ± 2.56	1.18 ± 0.11	16.8 ± 1.25	0.619	4.57 ± 0.15	692 ± 31
Ceriops decandra	35.68 ± 2.00	0.89 ± 0.058	0.080 ± 0.006	32.8 ± 1.58	1.88 ± 0.68	32.4 ± 1.58	1.7 ± 0.09	37.82 ± 2.13	1.219	5.56 ± 0.21	693 ± 40
Aegialitis rotundifolia	40.07 ± 1.91	0.325 ± 0.112	0.090 ± 0.004	24.5 ± 2.00	1.51 ± 0.44	62.5 ± 3.12	2.58 ± 0.46	10.5 ± 0.85	0.209	2.03 ± 0.08	639 ± 26
Xylocarpus granatum	35.68 ± 1.25	0.325 ± 0.103	0.090 ± 0.007	34.4 ± 1.98	0.98 ± 0.36	27.36 ± 2.12	1.14 ± 0.07	37.2 ± 1.15	1.401	2.03 ± 0.06	617 ± 50
Heriteira fomes	32.05 ± 2.56	0.508 ± 0.075	0.149 ± 0.012	56.0 ± 3.25	10.48 ± 2.85	24.56 ± 1.85	0.47 ± 0.06	42.4 ± 2.14	1.745	3.18 ± 0.09	567 ± 53
Sonneratia apetala	39.68 ± 2.68	0.345 ± 0.036	0.240 ± 0.018	31.3 ± 3.35	1.36 ± 0.28	20.51 ± 2.22	0.69 ± 0.07	33.4 ± 1.65	1.662	2.16 ± 0.14	566 ± 15
Bruguiera gymnorrhiza	40.45 ± 1.68	0.46 ± 00.026	0.031 ± 0.032	28.6 ± 2.95	1.79 ± 0.32	29.79 ± 1.00	1.66 ± 0.05	45.28 ± 1.85	1.575	2.88 ± 0.10	505 ± 85

3.3. Carbon sequestration rates

The annual increment of dbh exhibited a net accumulation of carbon from 0.088 to 0.171 μg C kg^{-1} AGB s^{-1} in the form of live biomass. Rates of carbon sequestration varied widely among species (Fig. 1). Mangroves with greater density sequester carbon at higher rate (0.156–0.171 μg C kg^{-1} AGB s^{-1}) than those with lower density (0.088 and 0.092 μg C kg^{-1} AGB sc^{-1}). This is in agreement with hardwood *Avicennia marina* which shows higher CO_2 assimilation rates relative to *Rhizophora sp*. and *Brugueira sp*. (Alongi, 2009). The change in the carbon stock (C) in mangroves (in terms of μg carbon sequestration per kg above ground biomass per second) exhibits positive relation with its density ($C = -0.118 + 0.000392\rho$, $R^2 = 78.7\%$, $F = 18.48$, $p = 0.008$). This indicates that heavier-wooded mangroves sequester more carbon than lighter-wooded mangroves.

3.4. FTIR spectroscopy

FTIR spectroscopy of different mangrove wood species along with one cellulose standard is shown in Fig. 2. Because of their complexity, bands were separated into two regions; the OH and CH stretching vibrations in the 3800–2700 cm^{-1} and the finger-print region which is assigned to different stretching vibrations of different groups from wood components in 1900–800 cm^{-1} (Table 3). According to the literature (Kondo, 2005) bands in the 3800–2700 cm^{-1} are assigned to inter and intra molecular hydrogen bonded (O—H) stretching absorption and prominent C—H stretching absorptions in cellulose and lignin. The intermolecular hydrogen bonds involving C6 positions (primary hydroxyl group) in lignin results in the formation of crystalline regions and contribute to the O—H bond at 3419/3351.These bands show a variation of maxima with a few wave numbers to a lower value in the spectra of *A. alba* (3367 cm^{-1}), *A. rotundifolia* (3368 cm^{-1}), *X. granatum* (3366 cm^{-1}) with density greater than *H. fomes* (3419 cm^{-1}) and *B. gymnorrhiza* (3400 cm^{-1}).

The spectra are very complex in the finger-print region (199–800 cm^{-1}). The position and relative intensity are different in different mangroves. The range of bands at 1633–1597, 1506–1517, 1206–1243 cm^{-1} are assigned to C=C, C—O stretching or bending vibration of different groups from lignin. The bands at 1441–1463, 1427–1441, 1320–1334, 1206–1246, 1111–1113 cm^{-1} are assigned to characteristic C—H, C—O deformation, bending or stretching vibration of different groups for lignin and carbohydrates. The bands at 1728–1739, 1375–1384, 1159–1161, 1035–1057 cm^{-1} are assigned to characteristic C=O, C—H, C—O—C, C—O deformation or stretching vibrations of different groups from carbohydrates (Popescu, Popescu, Lisa, & Sakata, 2011). Lignin and carbohydrate ratio were greater in *H. fomes* (1.75), *S. apetala* (1.66), *B. gymnorrhiza* (1.575) and *X. granatum* (1.4) than *A. alba* (0.230), *A. marina* (0.619) *A. rotundifolia* (0.209) as is evident from the increase of the 150.6–1517 cm^{-1} band height assigned to lignin and decrease of the 1728–1739 cm^{-1} band height assigned to carbohydrate. The ratio of the %*T* between 1506–1517 and 1728–1739 is decreased from 1.0857–1.0112 to 0.9497–1.0208 which shows a decrease in lignin content.

FTIR spectroscopy can offer the possibility of a quantitative cellulose determination in wood. Attempt has been made to correlate band at 4000–2500 cm^{-1} and 1700–800 cm^{-1} found in the FTIR spectra with cellulose concentration and following equation describes well the relation between cellulose content and the area of the bands ($R^2 = 93.4$, $F = 7.05$, $p = 0.257$)

$$\%Cellulose = 4.83 + 0.00568\,(4000 - 2500\,\mathrm{cm^{-1}}) - 0.00439\,(1700 - 800\,\mathrm{cm^{-1}})$$

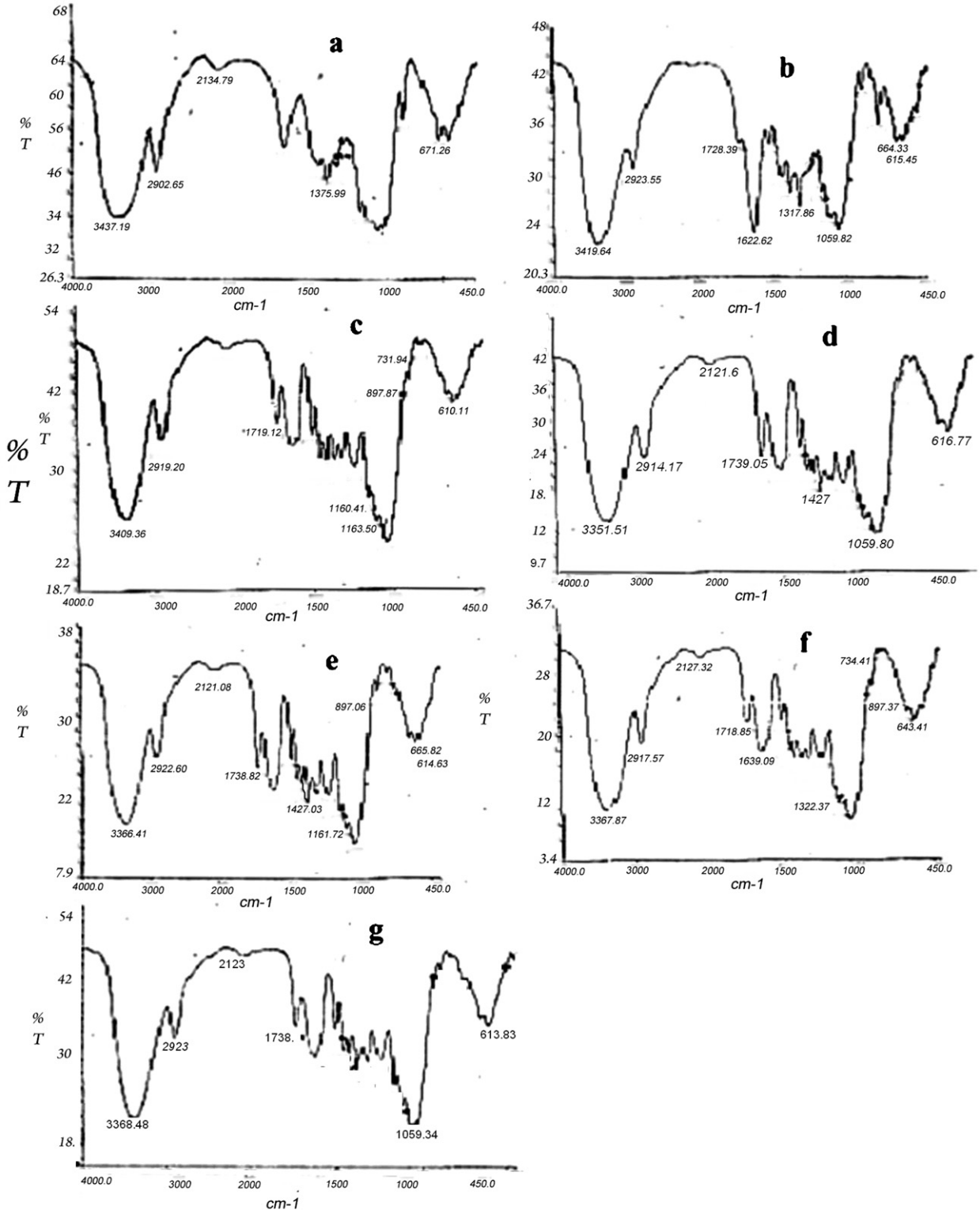

Fig. 2. FTIR scan of six mangrove wood species: (a) cellulose standard, (b) *Heriteira fomes*, (c) *Bruguiera gymnorrhiza*, (d) *Sonneratia apetala*, (e) *Xylocarpus granatum*, (f) *Avicennia alba*, (g) *Aegialitis rotundifolia*.

Table 3
Band assignment of FTIR of six mangrove wood species.

Wood sample	Cellulose peaks	Lignin peaks
Avicennia alba	3367, 2917, 1738, 1639, 1462, 1427, 1159, 1112, 1055, 897	1506, 1332, 1245, 834
Aegialitis rotundifolia	3368, 2923, 1738, 1463, 1427, 1161, 1113, 1035, 896	1627, 1507, 1320, 1243
Bruguiera gymnorrhiza	3400, 2912, 1739, 1639, 1375, 1160, 1113, 1054, 897	1597, 1508, 1331, 1245, 831
Sonneratia apetala	3351, 2914, 1739, 1384, 1161, 1113, 1057, 897	1627, 1506, 1321, 1246, 829
Heriteira fomes	3419, 2923, 1728, 1441, 1161, 1111, 1059, 894	1622, 1517, 1317, 1206, 781
Xylocarpus granatum	3366, 2922, 1738, 1463, 1427, 1161, 1113, 1057, 897	1633, 1506, 1320, 1246, 829

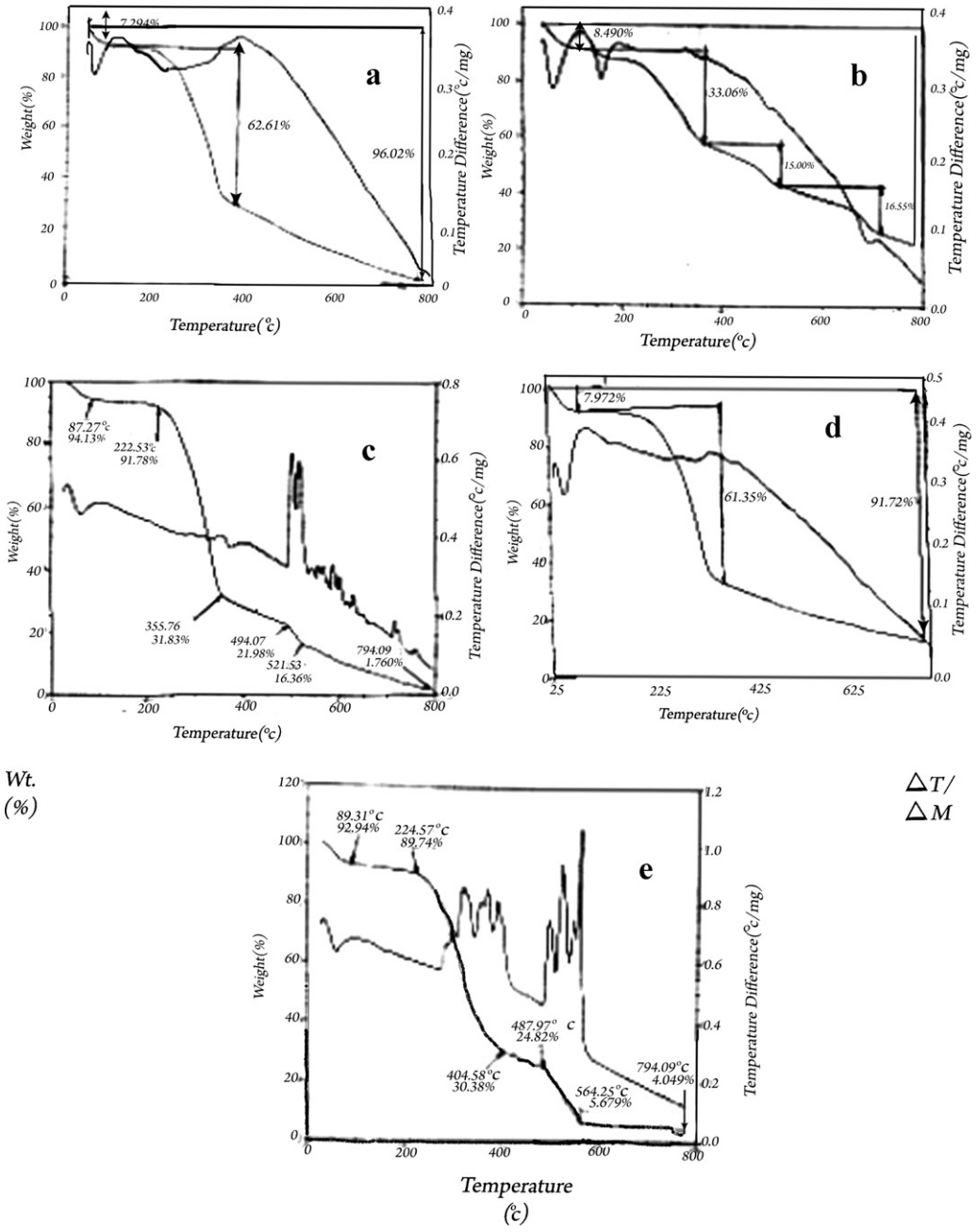

Fig. 3. TGA–DSC curve of different mangrove wood species: (a) *Avicennia alba*, (b) *Heriteira fomes*, (c) *Bruguiera gymnorrhiza*, (d) *Aegialitis rotundifolia*, (e) *Sonneratia apetala* (wt%: weight% and $\Delta T/\Delta M$: temperature difference, °C/mg).

Table 4
Thermogravimetric data (T_i, onset temperature, T_m, maximum decomposition temperature, T_{sh}, temperature at shoulder, T_f, final decomposition temperature, CV, calorific value and FVI, fuel value index for the mangrove wood samples (% of means of wt. loss in parenthesis).

Mangroves	T_i (°C)	T_m (°C)	T_{sh} (°C)		T_f (°C)		CV (MJ/kg)	FVI
Avicennia alba	96.2 (7.3)	377 (62.6)			788 (98)		19.	985
Heriteira fomes	111.4 (8.5)	358.2 (41.52)	515.2 (56.5)		715.2 (73)	796.2 (77.8)	15	1583
Bruguira gymnorrhiza	87.3 (5.9)	355.8 (68.2)	494.1 (78)	521.5 (83.6)	794 (98)		20	3922
Aegialitis rotundifolia	90.8 (7.97)	375.6 (61.35)			786.4 (91.7)		19	1509
Sonneratia apetala	89.3 (7.1)	224.6 (10.79)	487.97 (70)	564.2 (82)	794.1 (95)		19	3020

Table 5
VARIMAX-rotated factor loading matrices for cellulose and lignin with micrometeorological parameters.

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Communality
Density	**0.830**	−0.008	0.052	**0.307**	−0.243	0.844
Lignin	**−0.903**	−0.108	0.254	−0.066	0.104	0.907
Carbohydrate	0.282	0.113	**−0.885**	−0.151	−0.256	0.964
CO_2 (ppmv)	0.100	0.051	**0.790**	**−0.484**	−0.305	0.964
Air temp.	**−0.420**	**−0.871**	−0.108	0.075	−0.006	0.952
Rainfall	0.209	**−0.905**	0.175	−0.141	0.189	0.949
Humidity	0.280	0.070	−0.050	**0.947**	0.046	0.985
Solar rad.	0.226	0.134	−0.041	−0.062	−0.940	0.959
Variance	1.9425	1.6274	1.5218	1.2828	1.1502	7.5247
% Var	24.3	20.3	19.0	16.0	14.4	94.1

Bold values are statistically significant.

Calculated value obtained from the FTIR spectra are in very good correlation with the observed values of cellulose in different wood records ($R = 0.84$, $t = 3.48$, $p < 0.02$) (Table 2).

3.5. Thermogravimetry

As can be observed from Table 4 and Fig. 3, for the mangrove samples the onset temperature (T_i) for first step mass loss ranges between 87.3 and 114.4 °C and mass loss for this process varies between 5.9 and 8.5. This could be due to the devolatilization of the different low molecular weight compound from wood samples. The temperature corresponding to maximum decomposition temperature (T_m) decreases from 377 to 355 °C with decreasing density and are associated with the increase of FVI from 985 to 3922. The hemicellulose and or amorphous cellulose decomposition step appear as shoulder (T_{sh}) instead of well defined peak. In Ghana, Mainoo and Ulzen-Appiah (1996) observed the range from 1255 to 2488 as fuel value index (FVI) for the fast-growing species (*Leuceana leucocephala*, *Gliricidia sepium*, *Senna slamea*). In this study calorific values (CV, MJ/kg) of different mangroves were as follows: *Avicennia alba*, 19; *Heriteira fomes*, 15; *B. gymnorrhiza*, 20; *Aegialitis rotundifolia*, 19; *Sonneratia apetala*, 19.

The observed variability in the chemical composition and the micrometeorological parameters are used in VARIMAX rotated factor analysis and the results are given in Table 5. It shows the communality of the factor analysis that expressed the percentage of elements variability explained by the factor model and given the variance explained by each retained factor. Factor loading larger than approximately 0.3 are considered statistically significant (Chatterjee et al., 2006). The five factor model can explain 94.0% of the data variance. The first and the fourth factors have high loading and can account 24.3% and 16.0% response of total variance. Association of density, lignin and air temperature in the factor 1 and density, CO_2 and humidity in the factor 4 indicate significant effect of temperature on wood density and lignin content of the wood. Elevated temperature can significantly increase total lignin concentration and this is also reported that increase in lignin concentration is associated with decrease in cell wall thickness found in Scots pine during the longer growing season in response to the elevated temperature (Gindl et al., 2000; Peltola, Kilipelainen, & Kellomaki, 2002). Again carbohydrate and density in association with CO_2 show significant loading in both factors 2 and 4 indicate the combined effect of CO_2 and temperature on density. Scientists observed that density is related with chemical constituents (lignin and cellulose) of wood (Diaz-Vaz et al., 2009; Nuopponen et al., 2006) and Kilpelainen et al. (2003) reported that elevated temperature and CO_2 could affect wood properties resulting changes in wood density.

4. Conclusion

Mangroves exhibit wide fluctuations of carbon sequestration, showing an increase with increase wood density. Fourier transform infrared (FTIR) can be used to indirectly measure the cellulose which decreases with the decrease of density and increase of lignin. The increasing lignin concentration attributed to elevated fuel value index (FVI) is also a matter of economic interest. Future studies in mangrove wood chemistry hold the potential to provide seasonally resolved multidecadal CO_2, temperature, cellulose, lignin and density records, helping to fill a critical gap in mangrove ecology.

Acknowledgments

The authors gratefully acknowledge the support from the funding agency, Department of Science and Technology, New Delhi. The authors are indebted to Dr. Kumaresh Ghosh, Dept. of Chemistry, Kalyani University for encouraging to use FTIR during research and Dr. Pradyut Ghosh, Dept of Inorganic Chemistry, Indian Association for The Cultivation of Science, Kolkata, for guiding in TGA-DSC experimentation. Thanks are also due to Sundarban Biosphere Reserve and Divisional forest office, South 24 Parganas, Govt. of West Bengal for giving permissions to bring required mangrove samples for the experiment.

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