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Pyrolysis of forest biomass residues: comparative study of shimbal, cokad, cheed and cerus

Bijoy Biswas[a,b], Gaurav Mundada[a], Bhavya B Krishna[a,b], Rawel Singh[c], Jitendra Kumar[a], Thallada Bhaskar[a,b*]

[a]*Thermo-Catalytic processes Area (TPA), Material Resource Efficiency Division (MRED), CSIR-Indian Institute of Petroleum (IIP), Dehradun 248005, India*
[b]*Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India*
[c]*Department of Chemistry, A.S. College, Samrala Road, Khanna, 141402, India*

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ABSTRACT

In this work, pyrolysis of shimbal (SH), cokad (CO), cheed (CH), and cerus (CE) biomass were carried out at temperatures 350, 400, 450, and 500°C using a fixed bed reactor. The products yields as well as the characterization of the products were compared. The maximum bio-oil yield was observed at 500°C for SH (52.0 wt.%), at 450°C for CO (55.0 wt.%), at 450 °C for CH (52.0 wt.%) and at 450°C for CE (50.0 wt.%) biomass. The highest bio-oil yield was obtained in the case of CO biomass (55.0 wt.%) at 450°C compared to SH, CE and CH forest biomass residues. The obtained products were characterized by using GC-MS, ^{1}H-NMR, FT-IR, TOC, XRD, SEM instruments. The bio-oil mainly composed of phenols, furans, ketones, carboxylic acids and their derivatives. The distribution of compound was dependent on the biomass composition and decomposition temperature during pyrolysis. The phenolic compounds majorly present in all the bio-oils were mainly due to lignin degradation. Aromatic proton percentage highest was obtained for CO bio-oil ca. 27% while lowest was found in CE bio-oil. The carbon conversions of all biomasses were increased as the temperature increases from 350 to 500°C. Moreover CO biomass showed highest carbon conversion (60.57%) at 500 °C. Bio-char analysis showed that the CO, and CE bio-chars were rich in aromatics structure compared to the SH and CH bio-chars.

1. Introduction

Energy generation from non-edible biomass has been considered as a crucial step in reducing greenhouse gas emissions (Hall et al., 1998). Biomass as the energy source in substitution for fossil fuels has the potential to decrease the environment pollution, carbon emissions and global warming (Ahtikoski et al., 2008; Saidur et al., 2011). India produces 500 million tons of lignocellulosic biomass per year and Uttarakhand in India is a hilly state where more than 61.0% of forest biomass is produced. The forest biomass is generated ca. 4559.3 kT/Yr out of which ca. 3055.5 kT/Yris surplus biomass (Biomass resource, 2004). Currently, most residues are burnt thereby polluting the environment and also results in wastage of precious carbon. Therefore, developing a way to convert waste biomass into beneficial bio-energy efficiently has merit (Perlack et al., 2005; Stals et al., 2013).

Pyrolysis is the process of conversion of organic material to solid, liquid and gaseous products in the absence of oxygen and is being explored comprehensively in recent years (Ding et al., 2018; Kumagai et al., 2015). The products profile is changes concerning the process parameters used and hence can be used to meet the end user requirements easily. This way effective usage of wastes takes place in an environment-friendly manner (Mohan et al., 2006. Drastic reduction of solid residue volume (Inguanzoet al., 2002) and production of high energy value bio-oil with byproducts of bio-char and gas, (Liu et al., 2011) is the advantages of pyrolysis over other thermo-chemical conversion. The co-products obtained such as bio-char and gas by the pyrolysis have been used for energy production that further to the economic viability of the process (Biswas et al., 2017; Sotoet al., 2008; Krishna et al., 2016).

Forest industries as well as the typical forests were produced a huge amount of forest residues or surplus which can be shown to be potential feedstocks for pyrolysis into valuable products. Oasmaa et al., investigated the pyrolysis of forest and non-forest biomass residues at temperature of 480-520 °C and they showed that the highest bio-oil yield (62 wt %) was obtained with pine sawdust and lowest was observed (36-45 wt %) with straws and hay biomass. Pyrolysis of woody biomass resulted in better quality bio-oil which could be upgraded to transportation fuels or used for combined heat and power (Oasmaa et al., 2010). Pyrolysis of pine wood, pine bark, oak wood, and oak bark was carried out by Ingram et al. at 450 °C and they observed that liquid yields are partially dependent on very rapid heating of the wood particles to the final pyrolysis temperature (Ingram et al., 2008). The softwood bark residue was examine by pyrolysis by Chaala et al.in a continuous feed pilot-plant unit and it generated 26.1 wt.% bio-oil, 27.6 wt.% charcoal, and 27.4 wt.% gas (Chaala et al. 2004). In our previous research Krishna et al. carried out pyrolysis of deodar under a nitrogen atmosphere at different temperature 300, 350, 400 and 450 °C. They observed that at lower temperature 350 °C, the yield of bio-oil was highest (46.6 wt.%). Further increased in temperature to 450 °C, the bio-oil yield decreased and gas product

* Corresponding Author: *: tbhaskar@iip.res.in; thalladab@yahoo.com*

increased (Krishna et al., 2016). Biswas et al. investigated the pyrolysis of pine wood biomass at different temperature (300, 350, 400, 450, 500 and 550 ºC). They observed that the maximum bio-oil yield 58 wt.% at 500 ºC and the bio-oil majorly consisted of phenolic compounds (Biswas et al., 2016a). In case of wood catalytic pyrolysis using calcium-based materials studied in an auger reactor at 450 °C, it was noted that catalyst addition increased the organic phase formation versus the non-catalytic process from 27% to 34% and 31% for CaO and CaO-MgO, respectively (Veses et al., 2014). Pyrolysis of different kinds of straws (Oasmaa et al., 2010 ; Greenhalf et al., 2013) grass (Oasmaa et al., 2010; Greenhalf et al., 2013; Heo et al., 2010; Haarlemmer et al., 2016) and short rotation coppice (Greenhalf et al., 2013) have also been carried out so far. Haarlemmer et al. studied the pyrolysis of beech wood at different temperatures ranging between 450 ºC and 600 ºC. The pyrolysis tests residence time was between 60 and 90 min. The formation of bio-oil reached a highest of 62.4% at 500 ºC while the bio-oil yield decreased at higher temperature (Haarlemmer et al., 2016). Efika and co-workers examined the pyrolysis of biomass components such as cellulose, hemicellulose, and lignin and wood biomass at 800 °C with different heating rate (5 ºC min^{-1} to 350 ºC min^{-1}) on the products yields in a horizontally fixed-bed reactor. They showed that the maximum bio-oil (65.4%) and solid char (43.7%) yield for cellulose biomass and lignin with heating rate of 90 and 5 °C min^{-1} (Efika et al., 2018).

There are very few direct comparisons of pyrolysis between different wood biomass. However till now there is no report on the pyrolysis of typical Indian forest biomass residues and their comparisons on the products yield and products characterization. The novelty of this work is to explore the experimental data and evaluating the pyrolysis process for the forest biomass into valuable products. The main focus is characterization of bio-oil and bio-char which is useful for the production of chemicals/fuels and solid carbon catalyst. The pyrolysis experiments were carried out at different temperature 350, 400, 450 and 500 °C in nitrogen atmosphere. The obtained products such as bio-oil and bio-char were characterized using various analytical techniques such as Nuclear Magnetic Resonance Spectroscopy (NMR), Fourier Transform-Infrared Spectroscopy (FT-IR), Gas Chromatography- Mass Spectrometry (GC-MS), X-ray Diffraction (XRD) and scanning electron microscope (SEM).

2. Materials and methodology

2.1 Materials

Forest biomass such as Shimbal (English Name:Silk cotton, Scientific Name:Bombax ceiba), Cerus (English Name:Cedar, Scientific Name:Cedrus), Cheed (English Name:Pine, Scientific Name:Pinus) and Cokad (English Name:Oak, Scientific Name:Quercus) were collected from Dehradun district,Uttarakhand, India. All the forest residues were sun dried and residues particle size werebetween 0.5 and 2 mm.

2.2 Characterization methods

Thermal analysis of the forest biomass feeds were studied through thermogravimetric analysis (TGA) in a DTG 60 unit (Shimadzu, Japan). 2-5 mg biomass sample was placed in a sample pan and then heated from ambient to 900°C under N_2 flow at a heating rate of 10 °C/min. Elementar *vario* micro cube unit was used for the analysis of elements (CHNS) presents in the biomass feed. HR-83 Mettler Toledo Halogen Moisture Analyzer was used for the analysis of moisture content of the biomass. For the moisture analysis temperature was taken 105 ºC. Types of protons present in the bio-oils were characterized in Bruker Avance 500 Plus instrument using $CDCl_3$ as a solvent. The functional compounds present in the bio-oils have been analyzed by the help of gas chromatography–mass spectrometry (GC/MS Agilent 7890 B). Helium (He) used as a carrier gas; flow rate of the gas was 1 ml min^{-1}; HP-1 column (25 m × 0.32 mm × 0.17 μm). The column was heated from 50 °C to 280 °C with a heating rate of 5 °C min^{-1} and it was held for 5 min. 0.4 μL bio-oil was injected in a splitless mode. Nicolet 8700 FT-IR spectrometer with the sample diluted in KBr was used for the analysis of functional group present in biomass, bio-oil and bio-char. FEI Quanta 200 F, using tungsten filament doped with lanthanum hexaboride (LaB6) as an X-ray source, fitted with an ETD (Everhart Thornley Detector) was used for SEM images. XRD analysis of the biomass feed and bio-charwas done on Bruker D8 advance X-ray diffractometer fitted with a Lynx eye high-speed strip detector and a Cu Kα radiation source with a 0.04 step size (step time= 4s). Shimadzu TOC-L unit with solid sample module SSM-5000A was used for the analysis of total organic carbon (TOC) of raw biomass and bio-char. The proximate analysis, i.e., ash, volatile and fixed carbon percent were measured by placing a sample in a muffle furnace similar to ASTM D3175 method. Ash content was analysis by burning the biomass sample at temperature 575 ºC for 3 hour. However the volatile was calculated at 900 ºC with holding the sample for 5 minute.

2.3 Experimental procedure

The pyrolysis experiments were performed under a nitrogen gas flow in a fixed bed reactor with an internal diameter of 34 mm and a total length of 280 mm. 10 g biomass feed was taken in the reactor, in each experiment, and heated up to desired temperature (350, 400, 450 and 500 ºC) with a rate of 20 ºC min^{-1}. N_2 gas was used as a carrier gas. The reaction time was kept one hour at desired temperature. The pyrolysis products consisted of gasses, aqueous phase, organic phase (oil) while the solid bio-char remained at the bottom of the reactor. The condensable-gaseous were condensed at 5 °C in a water-cooled condenser and then collected. The organic phase was separated from the aqueous phase by using organic solvent diethyl ether. Its final amount was considered for calculation of product yield. The amount of gas was determined by the difference of bio-oil and bio-char yields. All the equations for the calculation of products yield were given below (Biswas et al., 2016).

$$Bio\text{-}oil\ \ yield, wt.\% = \frac{(W_4) - (W_3)}{\text{Weight of feed}} \times 100$$

$$\text{Bio-char yield, wt.\%} = \frac{(W_2) - (W_1)}{\text{Weight of feed}} \times 100$$

$$Gas\ yield, wt.\% = 100\% - (\text{Bio-oil yield, wt.\%} + \text{Bio-char yield, wt.\%})$$

$$\text{Conversion, \%} = 100\% - (\text{Bio-char yield, wt.\%})$$

Where. W_1=Weight of empty reactor, W_2=Weight of reactor after reaction, W_4=Weight of measuring cylinder with biooil, W_3=Weight of empty measuring cylinder.

The experiments have been carried out in duplicates and the average values have been reported which are within the standard deviation of ± 1.0%.

3. Results and Discussions

3.1 Characterization of forest biomass residues

The elemental analysis of the forest biomasses were revealed that the biomass mainly contains C, H and N and only trace amounts of S. The highest carbon content was determined to be for CE biomass (46.61wt.%) and lowest for CO biomass (44.34wt.%). Hydrogen content was found 7.47, 7.10, 7.81, and 7.64 wt % for SH, CO, CH and CE biomass respectively. Trace amounts of N and S were observed in all biomass as shown in Table 1. CH biomass had the highest volatile content (92.81wt.%), although CO was point uplowest volatile content, i.e., 87.83 wt.%. Ash content was low (less than wt. 6 %) for SH, CH and CE biomass while higher was observed for COi.e, higher than 8 wt.%. It has been seen that higher ash content biomass had higher the inorganic metal in the biomass (Kenney et al., 2013). Higher ash or inorganic metal present in the biomass seem to be potential to be have as a catalyst, and in-situ catalytic reactions are happened inside the reactor during thermal conversion (Kenneyet al., 2013). In Table 1 provided the calorific values of the biomasses. Maximum higher heating value (HHV) was observed in the case of CH biomass i.e. about 18.22 MJ/kg while the other three biomasses (SH, CO and CE) were showed similar HHV (ca. 17 MJ/kg).

Table 1. Ultimate and proximate analysis of Shimbal, Cokad, Cheed and Cerus forest

Elements	Ultimate analysis (wt.%)				Proximate analysis (wt.%)				
	C	H	N	S	Moisture	Volatiles	Fixed Carbon	Ash	HHV (MJ/Kg)
Shimbal	45.84	7.47	0.42	0.02	3.4	89.32	5.34	5.34	17.43
Cokad	44.34	7.10	0.40	0.01	3.9	87.83	3.68	8.48	17.12
Cheed	46.59	7.81	0.35	0.01	2.5	92.81	3.80	3.39	18.22
Cerus	46.61	7.64	0.28	0.01	2.6	92.56	4.61	2.84	17.55

To understand the thermal stability and pyrolytic behavior of forest biomasses, thermal analysis method (TGA/DTGA) is the most common and suitable technique. The thermal behavior of shimbal (SH), cokad

(CO), cheed (CH) and cerus (CE) forest biomass residue was analyzed and shown in Figure 1(a, b, c and d). The decomposition stages were different for different biomass, fundamentally because of their different compositions in the terms of content of moisture, cellulose, hemicellulose, and lignin. The first stage began at room temperature to 120 °C mainly due to weight loss of moisture. As the temperature was increased above 200 ºC, the mass loss rate increased and a maximum mass loss (ca. 39-55%) was observed at a temperature range of 250 and 400 ºC. It could be familiar to the disintegration of hemicelluloses and partially breakdown of cellulose and lignin (Popescu et al., 2011). The lignin present in the biomassis degrades along with some cellulose at higher temperatures of above 400 °C. At such high temperatures, fragmentation of their inter-unit linkages between the compositions also took place (Popescuet al., 2010). According to the TGA results, the maximum volatilization of hydrocarbons was occurred at temperature range of 350 to 500 ºC, and on the basis of this the pyrolysis temperature range for this study is appropriate.

The FT-IR functional groups presented in Table 2 of the forest biomass residues (SH, CO, CH, and CE) are attributed to the presence various functional group. This was mainly from the lignin, hemicellulose, and cellulose compositions in forest biomass. The large absorbance band at 3300-3450 cm^{-1} was attributed to the O-H group which comes from water or moisture content in the biomasses. The alkanes and alkenes C-H group were stretching vibrations bands observed at between 2890-2924 cm^{-1}(Siddiqui, 2010). The presence of hemicellulose carbonyl bond (C=O) is confirmed by the peak at 1720-1738 cm^{-1}. The bands at 1360-1410 cm^{-1} and 1200-1243 cm^{-1} were due to the CH_2 group symmetric deformation. The absorbance peak at 1100-1155 cm^{-1} attributed to the asymmetric deformation of C-O-C groups of the carbohydrates. The peak with higher intensity at 1000-1040 cm^{-1} was observed in the biomass which is related to the C-OH functional group stretching vibration. The absorption spectraof all the four forest biomass residues are showed likely similar.

Table 2. FT-IR functional groups at different stretching wave numbers.

Stretching wave numbers, (cm^{-1})	Functional groups
3200-3400	Alcohol O-H, Amines N-H, or Moisture
3000-3100	sp^2 C-Functional group
2850-3000	sp^3 C-H- Functional group
1700-1725	C=O stretch (Esters, Ketones, Aldehydes and Acids)
1600-1680	C=C stretch aromatic, N-H bend stretch
1200-1400	Acyl C-O, phenol C-O stretch
1000-1100	Alkoxy C-O stretch
700-900	Aromatic sp^2 C-H bend stretch
650-1000	Alkene sp^2 C-H bend stretch

3.2 Pyrolysis product yields

The mass balance of the products consisting of gas, bio-oil, and bio-charfrom pyrolysis of SH, CO, CH, and CEare presented in Figure 2 (a,b,c, and d). Maximum bio-oil yield was obtained at 500 °C for SH (52 wt.%) and at 450 °C with yields at 55, 52 and 50 wt.% for CO, CH, and CE respectively. In the case of SH, as the temperature increased from 350 to 500 °C, bio-oil yield increase not very significant and with further increased in the temperature the bio-oil yield decreases. Whereas with CO, CH and CE biomass the bio-oil yield was increased as the temperature increases from 350 to 450 °C but with further increasing in the temperature from 450 to 550 °C, the bio-oil yield decreased.The maximum pyrolysis bio-oil (55.0 wt.%) was found from CO biomass at 450 °C. However, bio-oil yield was diminished as the temperature increase from 350 to 500 °C, while the opposite trend was observed for gases yield. Moreover, the conversion (bio-oil and gas yield) of the reaction was seen to raises with an increases in reaction temperature. The higher conversionwas observed it might be due to the primary breakdown of carbohydrates and lignin at high temperature into smaller molecules (Biswas et al., 2016a). Researchers observed that as the temperature escalate to a certain level, maximum bio-oil is produced and that particular temperature is called as optimum condition or temperature (Krishna et al., 2016). Above the optimum temperature, bio-oil yield is became lower but increasing the non-condensable gas products yield,which is represents secondary bio-oil cracking of the vapour phase in the reactor during pyrolysis (Haarlemmeret al., 2016; Wuet al., 2014). Forest biomasses such as SH, CH, and CE

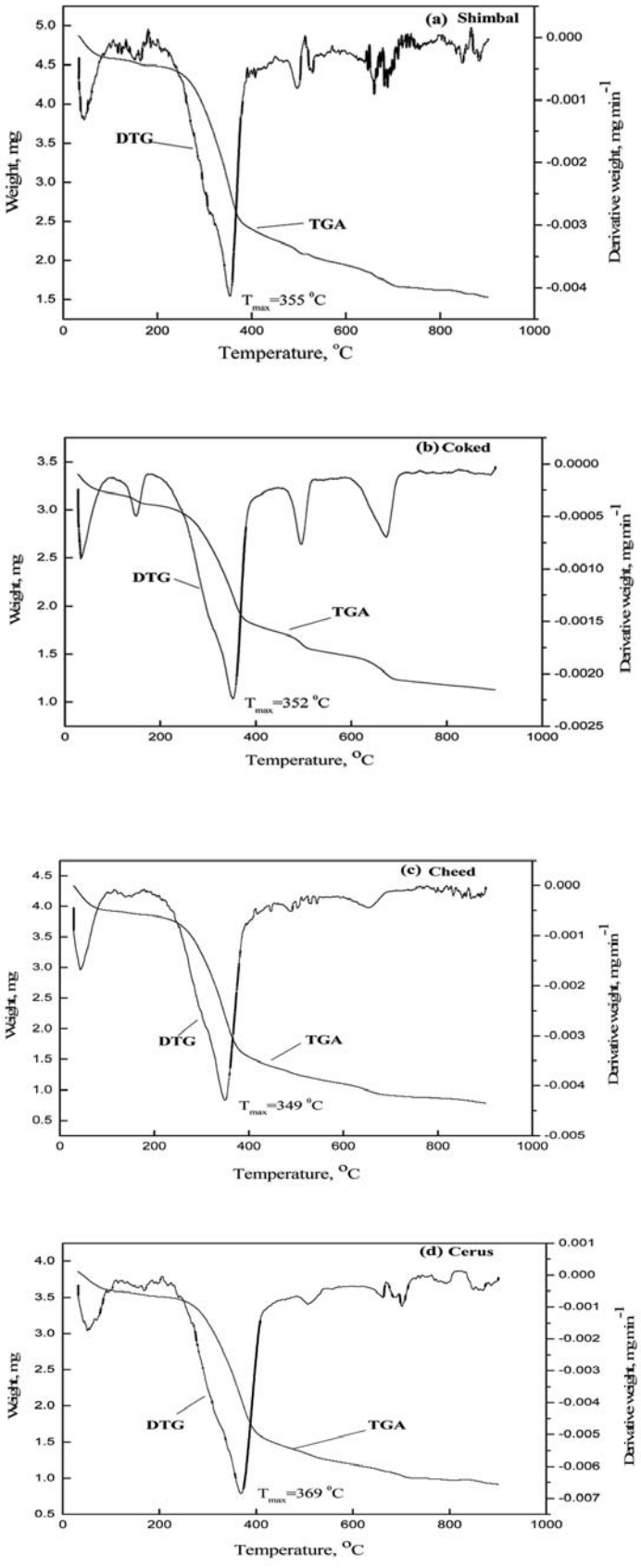

Figure 1:
TGA/DTG of (a) Shimbal, (b) Cokad, (c) Cheed and (d) Cerus forest biomass residues

were produced higher gas yield 23.0 24.0, and 26.0 wt.%, compared to the CO biomass gas yield (22.0 wt.%). The product yield behaviours are mainly depends on the conditions used i.e., type of biomass, type of reactor, and type of pyrolysis temperature (Wu et al., 2014). From mass balance results, we can understand that structural differences in the different biomass have a significant effect on product distribution as also evident from TGA and FT-IR characterization (Safdariet al., 2018). It is concluded that the optimum temperature for bio-oil production was 500 ºC for SH and 450 ºC for CO, CH and CE biomass in the presented experimental conditions. The forest biomass sources investigated here produced a desirable amount of bio-oil, which could be suitable for use as fuels/ chemicals industry feedstocks.

3.3 Bio-oil characterization

3.3.1 GC-MS analysis of bio-oil and reaction pathway into the compounds

The semi-quantitative analysis of the optimum condition bio-oils (SH-500, CO-450, CH-450, and CE-450 °C) were analyzed with GC-MS and shown in Table 3. The GC-MS is an important parameter for the identification of composition of the bio-oils. The macromolecule compositions (carbohydrates and lignin) of the biomass are decomposed during the pyrolysis produces a phenolic derivatives, ketones, aldehydes, carbohydrate-derived compounds, and nitrogen containing compounds. As seen from the Table 3, major compounds were observed in SH pyrolysis bio-oil at 500°C (SH-500) are Benzoic acid, 4-hydroxy-3-methoxy- (5.7%), Phenol, 2,6-dimethoxy-(4.7%), Phenol, 4-ethyl-2-methoxy- (4.1%), Phenol, 2,6-dimethoxy-4-(2-propenyl)- (4.5%), Benzeneacetic acid, alpha-hydroxy-2-methoxy- (4%) and 2-Methoxy-5-methylphenol (3.4%). For CO biomass at 450°C (CO-450) the main compounds were 4-Methoxy-2-methyl-1-(methylthio) benzene (5.9%), Phenol, 2-methoxy- (5.4%), Phenol, 4-ethyl-2-methoxy- (4.1%), Phenol, 2,6-dimethoxy-4-(2-propenyl)- (4.1%), Phenol, 2,6-dimethoxy- (4.8%), Homovanillic acid (4.2%) and 2-Methoxy-5-methylphenol (4.1%). 1,2,3-Trimethoxybenzene (5.5%), Phenol, 2,6-dimethoxy- (5.5%), 2-Methoxy-5-methylphenol (4.2%), Phenol, 4-ethyl-2-methoxy- (4.2%) and Phenol, 2-methoxy- (3.6%) were the compounds found in major concentration in bio-oil obtained from CH biomass at 450°C (CH-450). The major compounds observed from GC-MS of bio-oil derived from pyrolysis of CE biomass at 450°C (CE-450) were 4-Methoxy-2-methyl-1-(methylthio) benzene- (6.8%), Phenol, 2-methoxy- (5.2%), Phenol, 2,6-dimethoxy- (5.3%), Homovanillic acid (4.3%) and 2-Methoxy-5-methylphenol (4.4%). The common compounds were found in significant proportions in all the samples were 2-Methoxy-5-methylphenol (3.4%-4.4%), Phenol, 2,6-dimethoxy-4-(2-propenyl)- (3.2%-4.5%), Phenol, 2-methoxy- (3.5%-5.4%) and Phenol, 4-ethyl-2-methoxy- (3.6%-4.2%). 4-Methoxy-2-methyl-1-(methylthio) benzene was found in both CO-450 and CE-450 in high amounts of 5.9% and 6.8% respectively. These were the highest

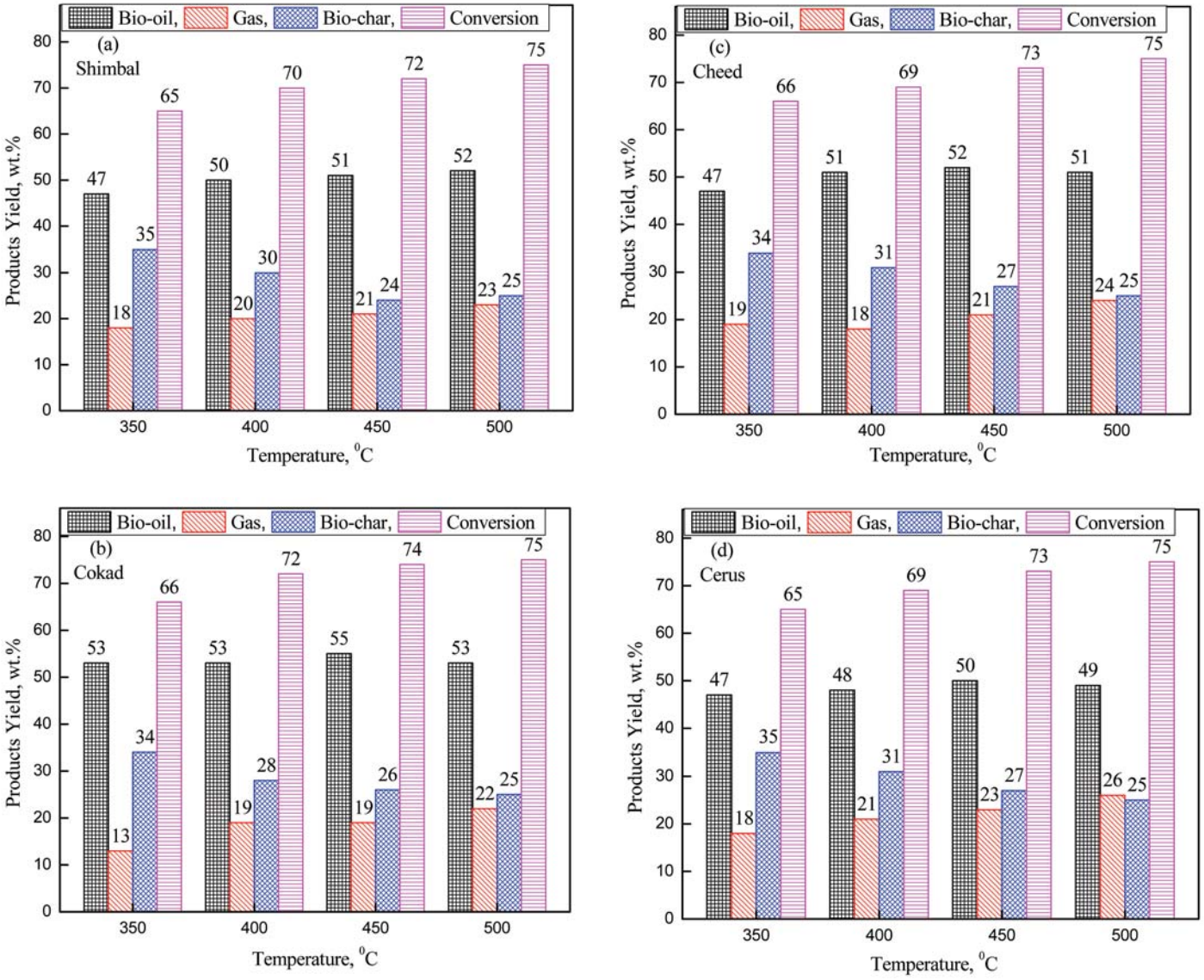

Figure 2: Effects of temperature 350, 400, 450 and 500 °C on products yield of (a) Shimbal, (b) Cokad, (c) Cheed and (d)Cerus biomass.

area percentage compoundout of all the compounds obtained from the bio-oils.

During pyrolysis, the carbohydrates and lignin α-O-4 bonds are broken first and make individual availability of carbohydrates and lignin (Gilletet al., 2017). In general, it was seen that phenolic compounds dominated in the all bio-oil which could be attributed to the high lignin content of forest biomass (Doumer et al., 2015). The cleavage of the β-aryl-ether bond (β-O-4) is the most important as predominate linkage in the lignin structure into the products (Santos et al., 2012; Biswas et al., 2016b). The different percentage of phenolic derivative compounds were obtained due to the lignin macromolecules degraded differently as they containa different percentage of β-aryl-ether, C-C, α-O-4, 4-O-5 and 5-5 bonds (Gillet et al., 2017). Furan derivatives compound mainly obtained from the hemicellulose decompositions in the biomass, which is shown by the different researcher group (Alvarez et al., 2014; Ding et al., 2018; Biswas et al., 2018b). The chemical components such as phenolic, aldehydes, ketones, and alcohol are also found in bio-oils derived from other feedstocks (Doumer et al., 2015).

Table 3: The chemical composition of Shimbal, Cokad, Cheed and Cerus bio-oil obtained from gas chromatography–mass spectrometry (GC/MS) at optimal conditions.

Compounds identified in bio-oils	Area, %			
	SH -500 °C	CO-450 °C	CH-450 °C	CE-450 °C
1,2,3-Trimethoxybenzene	-	-	5.5	-
1,2-Benzenediol, 3-methoxy-	2.0	2.3	-	2.6
1,2-Benzenediol, 4-methyl-	1.6	1.2	-	1.2
1,2-Cyclopentanedione	1.1	-	-	1.3
1,2-Cyclopentanedione, 3-methyl-	2.6	3.1	1.9	3.1
1,4-Pentadiene, 2,3,3-trimethyl-	1.5	-	-	-
2,3-Dimethoxytoluene	-	1.1	-	-
2',4'-Dihydroxypropiophenone	-	1.9	-	-
2,4-Hexadiene, 2,5-dimethyl-	-	-	-	1.5
2,5-Dimethoxy-4-ethylamphetamine	2.8	-	-	-
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	1.1	1.1	1.1	0.9
2-Furancarboxaldehyde, 5-methyl-	1.6	-	2.4	2.1
2-Furanmethanol	1.8	2.2	1.5	2.4
2-Methoxy-4-vinylphenol	2.8	3.4	3.0	3.4
2-Methoxy-5-methylphenol	3.4	4.1	4.2	4.4
2-Methyl-5-hydroxybenzofuran	0.6	-	-	1.0
2-Propenal, 3-(1,3-benzodioxol-5-yl)-	0.9	-	-	-
3-Allyl-6-methoxyphenol	-	1.2	-	-
4-Hydroxy-2-methoxybenaldehyde	-	-	2.3	-
4-Hydroxy-2-methoxycinnamaldehyde	2.0	1.9	2.6	1.4
4-Methoxy-2-methyl-1-(methylthio)benzene	-	5.9	-	6.8
4-Propyl-1,1'-diphenyl	-	-	1.3	-
5-tert-Butylpyrogallol	-	-	3.1	-
9,10-Dihydro-9-oxo-10-phenylanthracene	1.7	2.9	1.6	2.0
Apocynin	-	0.7	-	0.9
Aspidinol	1.1	-	-	-
Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	1.1	-	-	-
Benzeneacetic acid, .alpha.-hydroxy-2-methoxy-	4.0	-	-	-
Benzoic acid, 4-hydroxy-3-methoxy-	5.7	-	-	-
Catechol	2.9	1.0	0.8	1.9
Cyclopropane, 2-(1,1-dimethyl-2-pentenyl)-1,1-dimethyl-	-	-	1.3	-
Desaspidinol	2.2	-	2.4	2.0
Ethanethioic acid, S-phenyl ester	-	-	-	1.2
Eugenol	1.0	-	-	1.0
Furfural	2.9	3.2	2.1	3.7
Homovanillic acid	-	4.2	-	4.3
Homovanillyl alcohol	-	-	1.7	-
Phenol	1.8	2.3	1.0	2.2
Phenol, 2,4-dimethyl-	1.1	-	-	1.3
Phenol, 2,5-dimethyl-	-	-	1.0	-
Phenol, 2,6-dimethoxy-	4.7	4.8	5.5	5.2
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	4.5	4.1	3.4	3.7
Phenol, 2,6-dimethyl-	0.5	0.6	-	-
Phenol, 2-ethoxy-	-	-	1.2	-
Phenol, 2-methoxy-	4.2	5.4	3.5	5.2
Phenol, 2-methoxy-4-propyl-	2.3	-	-	1.7
Phenol, 2-methyl-	1.2	1.5	-	1.2
Phenol, 3,5-dimethyl-	0.6	1.3	-	0.6
Phenol, 3-methoxy-2,5,6-trimethyl-	-	-	1.4	-
Phenol, 4-(ethoxymethyl)-2-methoxy-	-	-	2.2	-
Phenol, 4-ethyl-2-methoxy-	4.0	4.2	3.6	3.9
Pyrazine, methoxy-	-	2.0	-	-
Toluene	-	1.7	-	1.6
trans-Isoeugenol	2.3	1.3	1.3	1.3

SH= Shimbal, CO=Cokad, CH=Cheed and CE=Cerus and 450 and 500 are the temperatures

3.3.2 Fourier transform-Infrared spectroscopy (FT-IR)

FT-IR spectroscopy was used to study the distribution of functional group types present in the pyrolysis bio-oils and which is shown in Table 2. Most of the functional groups were observed in the bio-oils such as O-H, C=O,-CH_2, -CH_3,C=C and -C-O groups (Krishna et al., 2016). O-H stretching vibrations of the phenolic and alcoholic compounds were observed at 3402 cm^{-1} (Jiang et al., 2018; Krishna et al., 2016). The intensity of these bands are varies with the different forest biomass bio-oils. O-H stretching group was showed for CO-450 and SH-500 bio-oil while lower absorbance intensity was observed for CH-450 bio-oil. The bands between 3000 and 2900 cm^{-1} are for the C-H stretching vibrations (Safdari et al., 2018), and higher intensity peak was observed in all bio-oils indicating that they contain alkanes and alkenes groups. The aldehydes, ketones, carboxylic acids or esters compound's C=O stretching vibrations are observed at 1650-1714 cm^{-1}, and the same intensities were observed in all bio-oils (Jiang et al., 2018). The obtained bio-oils were showed the stretching vibrations at 1512-1640 cm^{-1} which is due to the aromatic compound (C=C) stretching. The bands peaks between the "fingerprint" regions (1500-550 cm^{-1}) were observed in the bio-oil. These peaks at the finger print region are demonstrated that the bio-oils consisting of many functional groups which are in good agreement with the GC-MS results. The CH_3 asymmetric and CH_2 scissoring vibrations stretching bands were endorsed at 430-1470 cm^{-1}. The bio-oils were showed maximum absorbance band at 1218 cm^{-1} which is allocated due to the C–O functional group. The lower frequency bands were displayed at 806-1150 cm^{-1} represent C–O, C–C; C–H stretching bonds which is due to acids, alkanes,and etc. groups (Jiang et al., 2018). Hence, the differences of absorbance peaks were observed in the bio-oils are due to the different compositions (carbohydrates, and lignin) present in the forest biomasses which are break into different functional chemicals.

3.3.3 ^{1}H Nuclear magnetic resonance (NMR)

Proton NMR spectra of bio-oils are shown in figure 3(a, b, c, and d). The region from 0.5 to 1.5 ppm showed the aliphatic protons that are bonded to the two bonds away from C=C or heteroatom containing protons. The higher percentage of protons (above 30.0%) was observed at 1.5 to 3.0 ppm region in the all bio-oils that is illustrated protons bonded to a C=C double bond. The overall aliphatic protons are represented in the region from 0.5 to 3 ppm (Siddiqui et al., 2009; Biswas et al, 2018a). In this region, a higher percentage of protons were observed in the case of SH, CO, and CH bio-oils compared to CE bio-oil. A Methoxyl or methylene group proton that joins two aromatic rings is observed from 3.0-4.5 ppm region (Kosa et al., 2011). All the bio-oils from SH, CO CH and CE were showed almost the same proton percentage ca. 21% in this region. The low percentage of methoxy/carbohydrate functionality protons (4.5-6.0 ppm) was observed inthe case of CE bio-oils than SH, CO and CH bio-oils.The aromatic functionality protons are found in the region from 6.0 and 8.5 ppm (Biswas et al., 2018b). Highest proton percentage was obtained in this region for CO bio-oil ca. 27% while lowest proton percentage was observed in case of CE bio-oil. The acidic and aldehydes protons are confirmed in all the bio-oils in the region from 8.5 to 10 ppm, which is also confirmed by the FT-IR analysis. A variety of functionality protons were observed from the NMR analysis that is in good agreement with findings from FT-IR analysis.

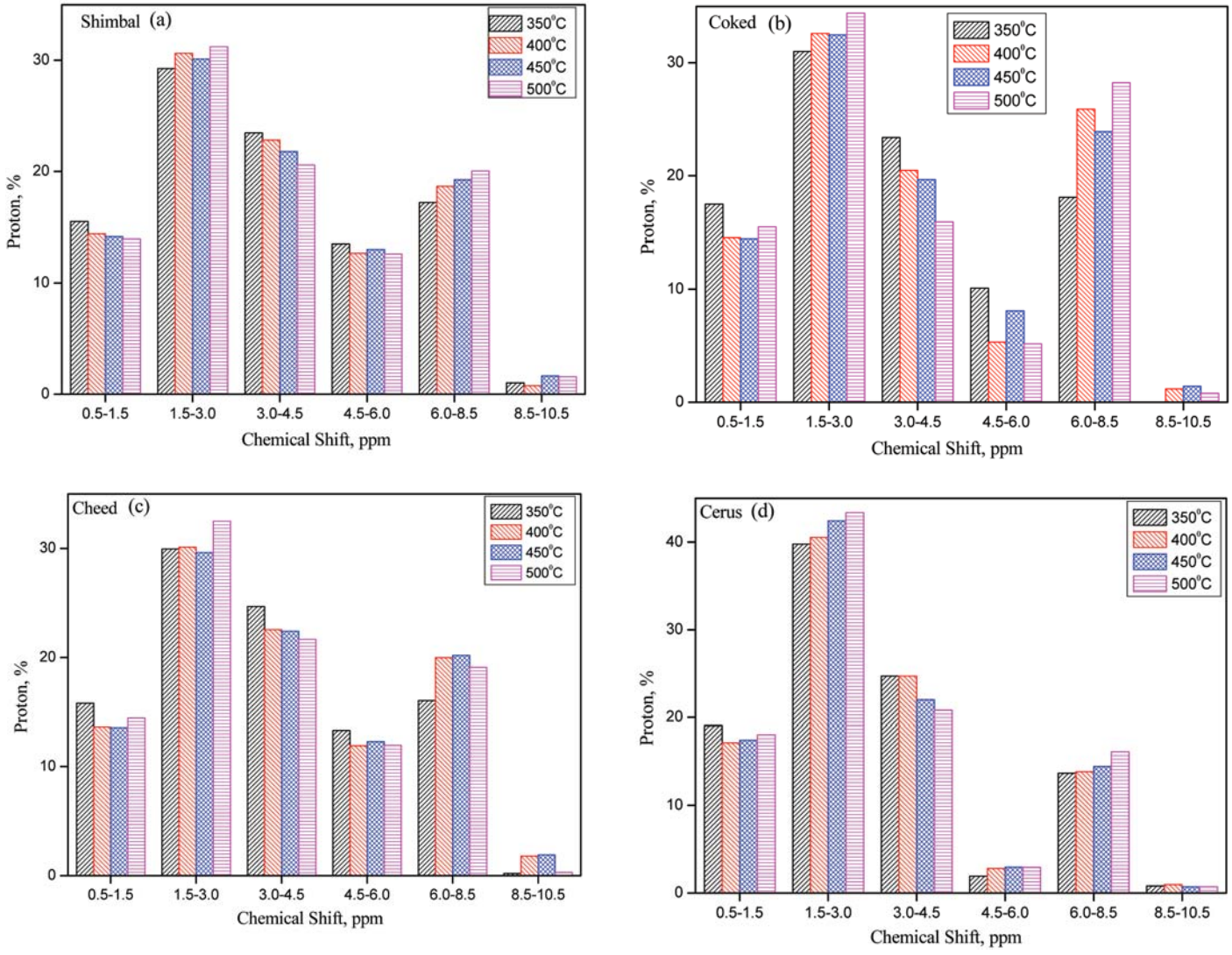

Figure 3: ^{1}H Nuclear magnetic resonance (NMR) of (a) Shimbal bio-oil, (b) Coked bio-oil, (c) Cheed bio-oil and (d) Cerus bio-oil.

3.4 Analysis of carbon conversion

The carbon conversion into products based on the carbon present in the biomass was investigated from the total organic carbon (TOC) analysis of each bio-char during the pyrolysis process. As can be seen in Figure 4, the carbon conversion was increased as the temperature increases from 350 to 500 °. At temperature 350 °C, the maximum carbon conversion (45.11%) was observed for the CH and CO biomass while lowest was found for SH biomass (43.02%). The highest carbon conversion are showed may be due to the CH contain higher volatile matter (92.81%) compared to the other three biomass. Although SH biomass has higher volatile matter than that of CO biomass, CO biomass showed higher carbon conversion compared to SH biomass due to CO had higher ash content (8.48%) which might be act as a catalyst (ash content) and was produced higher condensable vapor. As the temperature increased 350 to 400 °C, the carbon conversion some what increases, and the maximum was observed for CO biomass (51.06%). The maximum carbon conversion was obtained 53.12 % for CE biomass, and lowest (51.86%) was observed for SH biomass at 450 °C. The CO biomass showed highest carbon conversion 60.57% at 500 °C while at same temperature lowest carbon conversion was observed for SH biomass (53.49%). The lower carbon conversion observed for SH biomass may be due to the higher fixed carbon present in the SH biomass. Overall the carbon conversion into products was observed higher for CO biomass. This is indicated that the ash content in the biomass might be act as a catalyst and enhanced the products.

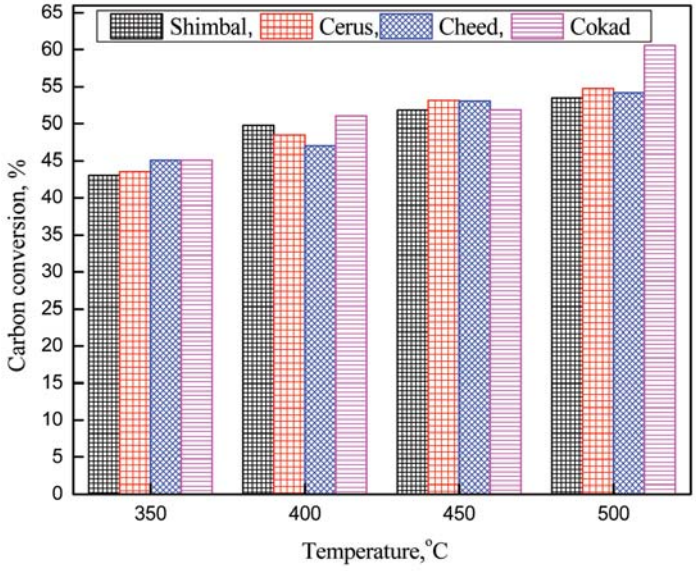

Figure 4: Analysis of Carbon conversion during pyrolysis of Shimbal (SH), Cokad (CO), Cheed (CH) and Cerus (CE) biomass.

3.5 Bio-char characterization

The structural changes during the pyrolysis of the biomasses were analyzed by the help of FT-IR spectra (Table 2). The peak at 3477 cm^{-1} assigned to O-H stretching vibrations indicates the presence of the oxygen-containing compounds (water or alcoholic O-H). SH and CE samples were showed broad peaks with maximum intensity at about 3477 cm^{-1} whereas CH and CO showed less intensity. The absorbance peak at 1580-1620 and 827 cm^{-1} were articulated to aromatic C=C and aromatic C-H functional group present in the bio-chars (Uzun et al., 2010). In this region CO, CH and CE derived bio-chars were showed higher intensity band while SH derived bio-char was showed lower intensity. The band at 1390-1422 cm^{-1} is assigned to C-H deformation. New absorbance peaks at a region between 1422 to1100 cm^{-1} appeared in all bio-chars due to the various substitute aromatic materials are present in the bio-chars. The obtained bio-chars are showed various functionalities mainly in the "fingerprint" region (1500-450 cm^{-1}).

XRD spectrum was used to determine the effects of temperatures on biomass compositions decompositions during pyrolysis. The results are shown in Figure 5(a and b). The dispersing diffraction peak angles (2θ) from 15 to 22°, in the case of both forest biomasses and bio-chars, were observed due to the cellulose and the aliphatic chain group. The crystalline peaks were observed in all forest biomass residues at 2θ = 22.22 °, which is characteristic of cellulose and turbostratic carbon (Xu et al., 2008). While these peaks vanishedin the pyrolysis bio-chars and a new XRD signals was detected at 2θ = 25.2°. The new peaks were indicated that coke/char occurred after pyrolysis. This is due to the decomposition of the cellulose and lignin matrix of the forest biomass residues into the products.The surface topographies of four forest biomass residues and pyrolysis bio-chars were studied using a scanning electron microscope (SEM). As seen in Figure 6, bio-chars hada lot of loose spongy structures and cracking of the surface. It indicated that bio-char might potential to be used for adsorption. This may help in promoting the commercial application of the pyrolysis of forest biomass residues.

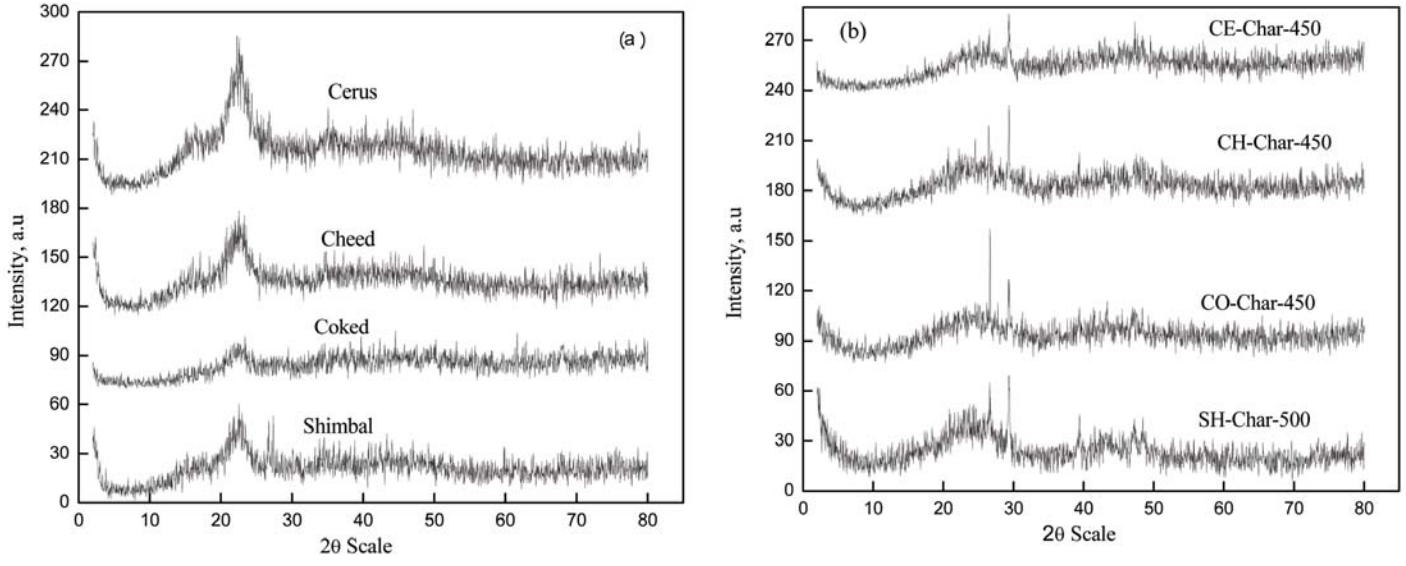

Figure 5: XRD spectra of four forest biomass(a) Shimbal, Cokad, Cheed and Cerus and (b) bio-char obtained at optimal temperature from pyrolysis of Shimbal, Cokad, Cheed and Cerus.

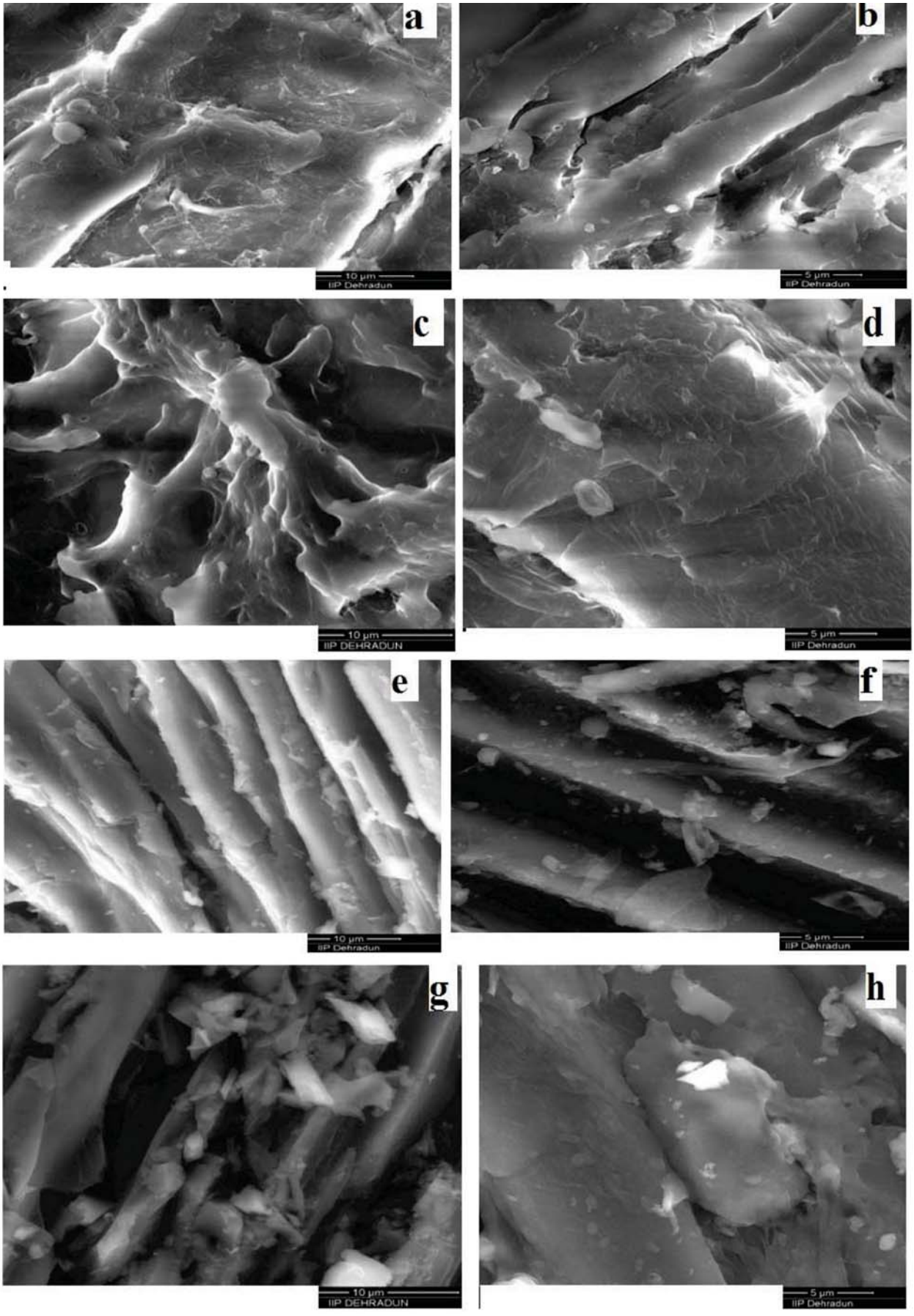

Figure 6: SEM of forest biomass residues Shimbal, Coked, Cheed and Cerus (a, b, c and d) and bio-char at 500 °C for Shimbal (e), 450 °C for Coked, Cheed and Cerus (f, g and h).

4. Conclusions

The pyrolytic behavior of different forest biomass with different temperature has been studied. The highest bio-oil yield of 55.0 wt.% was obtained with CO biomass residue at 450 °C than the other three forest biomass residues. Pyrolysis of forest biomasses are mostly produced polar oxygenated compounds which are due to the degradation of macromolecules (carbohydrates and lignin) present in the biomass. Phenolic compounds, acids, aldehydes, ketones, and furans are formed the wide variety of functional chemicals present in the obtained bio-oils. The obtained bio-oils could be used as fuels/chemicals, resins, and fertilizers, etc. FT-IR, SEM and XRD results of the biomasses and bio-chars indicated that the macromolecular forest biomass residues are broken down into bio-oil and gaseous product.

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