

Chapter 3 Characterization of charcoals produced from *Acacia*, *Albizia* and *Leucaena* for application in ironmaking

Charcoals produced from three hardwood species, *Acacia nilotica* (W1), *Albizia lebbek* (W2) and *Leucaena leucocephala* (W3), were evaluated as a reductant in ironmaking. Charcoals were produced with slow (5 °C/min) and fast heating rates (50 °C/min) at 600, 800 and 1100 °C. Charcoals were characterized using proximate analysis, ultimate analysis, volume shrinkage, compressive loading, scanning electron microscopy, Fourier transform infrared spectroscopy, Raman spectroscopy and reactivity towards CO₂, for their chemical, mechanical and physical properties.

3.1 Introduction

The level of CO₂ has risen to alarming level in the atmosphere and adverse effects of global warming and climate change have already started to threaten life on the planet. Iron and steel industries contribute approximately 7% of global CO₂ emission by burning fossil coal [125]. Also, coking coal reserves are depleting rapidly. It is about time we strictly reduce CO₂ emissions and switch to renewable energy sources in iron and steel industry. Biomass is a renewable and carbon-neutral energy source that can be grown commercially by short-rotation forestry. Also, having around 300 sunny days a year, fast production of hardwood biomass is favourable in the Indian climate [40].

As fuel and reductant, biomass poses some challenges, such as low energy density, hygroscopic nature and a high moisture content. Thermochemical processes such as carbonization can help remove these drawbacks, enabling the resulting charcoal to act as a suitable reductant in ironmaking. Several researchers have already worked on the carbonization of different biomasses and studied the properties of the resulting charcoals

for various applications. Griessacher et al. [126] carbonized agricultural residues up to a temperature of 1000 °C to assess the possibility of producing “metallurgical” charcoals (>85% of fixed carbon with low ash and volatile matter). The carbonization of olive stones, cork oak cuttings, olive tree cuttings, pruning, grapevines, fruit tree cuttings and grape marc were carried out in the temperature range of 400-1000 °C. Charcoals produced at more than 700 °C temperature had high carbon content. The charcoals reduced zinc and iron oxide to a higher extent than petroleum coke in reduction tests. Demirbas [127] carried out the carbonization treatments for the hazelnut shells, hardwood, and softwood in the temperature range of 550-1150 °C with a fixed heating rate of 10 °C /min. The authors reported that the yield of the hardwood charcoals decreases from 36 to 23% as temperature increases from 550 to 1150 °C.

Kumar et al. [90] studied the influence of carbonization temperature (400-1200 °C), soaking time (1-5 h) and heating rate on the chemical composition and yield (ratio of the weight of charcoal to wood) of chars prepared from *Eucalyptus* and *Acacia* woods. The authors reported that the charcoal yield is higher in case of slow heating. Charcoal from eucalyptus was reported to have slightly higher carbon content and charcoal yield. Paris et al. [97] studied the thermal degradation of wood biopolymers and evolution of atomic or molecular structure in pine and spruce biomass using wide and small-angle x-ray scattering and Raman spectroscopy in the temperature range of 25-1400 °C. Authors reported that above 423 °C stacking of 2D graphene sheets starts. Further, with rise in temperature, successive ordering of turbostratic carbon increases.

Qi et al. [128] investigated the carbonization properties of maize straw, cotton stalk and poplar wood in a nitrogen atmosphere at the maximum temperatures in the range of 300-800 °C for one hour. Authors reported that higher quality charcoals can be obtained by carbonizing at higher temperatures and H/C and O/C values decreased linearly as carbonization temperature increased. Yan et al. [129] investigated the influence of pyrolysis process parameters i.e., the

heating rate, temperature, flow rate, and the purge gas type on the yield of charcoal produced from pyrolysis of southern pine chips. The pyrolysis temperatures were in the range 450–1000 °C, with heating rates of 0.5, 1.0, 10, 30, 50, and 100 °C /min. Authors reported that the yield of pine char decreased as temperature and heating rate increased. Katyal et al. [130] carried out carbonization of sugar cane bagasse in a fixed bed reactor in order to determine the effect of process variables such as temperature (250–700 °C), heating rate (5–30 °C/min) and particle size on the composition and yield of produced charcoal. The authors reported that fixed carbon and ash content increased with increase in temperature. Authors further suggested that charcoals obtained at carbonization temperatures above 500 °C are suitable as renewable reductants.

Charcoals from hardwood biomass have favourable metallurgical properties, which can be used as a reductant in ironmaking processes [114]. Forestry biomasses contain fewer ash-forming elements than agricultural biomasses [131]. Thus, carbonization of forestry biomasses will yield low ash charcoal, which will minimize the slag volume and contamination in the melt during downstream processing of directly reduced iron (DRI). Benlliure et al. [132] characterized sixteen different tropical woods in Costa Rica. The authors characterized the charcoal produced at 450 °C using density, compression resistance, proximate analysis, gross calorific value, FTIR spectroscopy and thermogravimetric degradation. Along with the values for different tests, authors performed multivariate analysis by principal components and reported that up to 99% of the variation of said characteristics could be explained. Literature for the characterization of wood charcoal is in abundance [133]. In comparison, literature for characterization of the same in the context of iron and steelmaking is limited. Emmerich and Luengo [134, 135] characterized babassu charcoal to use in a blast furnace. Authors reported that babassu charcoal could substitute metallurgical coke in a high-capacity blast furnace. Dufourny et al. [136] characterized sprue and eucalyptus charcoal at different carbonization temperatures (500, 650 and 800 °C) and residence times (0 and 90 min) to evaluate their

suitability in ironmaking. Authors reported that spruce charcoal has higher mechanical strength, CO₂ reactivity, lower fixed carbon, charcoal yield and apparent density than eucalyptus charcoal.

Preliminary study suggests that up to 50 wt% of coal can be replaced with charcoal of similar particle size in pulverized coal injection in blast furnace [137]. Addition of 5-10 wt% charcoal with the metallurgical coal increases the resulted bio-coke reactivity without compromising the strength as compared with the metallurgical coke [43, 45]. Up to 25 wt% replacement of coke breeze with charcoal is possible in sintering without significant impact on the product quality [49]. Iron ore composite pellets using charcoal instead of coal as reductant has superior reduction characteristics [88]. The charcoal mini blast furnace is an established technology which uses granulated charcoal [138].

Fast growing and high carbon wood species which can produce high carbon charcoal with higher yield and calorific value are preferred in ironmaking industry. Plant species like *Acacia nilotica* (W1), *Albizia lebbbeck* (W2) and *Leucaena leucocephala* (W3) which thrive in temperate Indian climate condition, have been deemed as suitable candidates for charcoal production for metallurgical and power industries [39]. Short rotation forestry with these wood species has potential to reduce carbon emissions from iron and steel industry. In the present study, charcoals from these biomasses were produced at different carbonization temperatures and heating rates. Furthermore, the characteristics of the charcoals were compared with the conventionally used fossil-based coal and coke to demonstrate their applicability as a CO₂-neutral substitute in ironmaking.

3.2 Experimental

3.2.1 Preparation of Charcoals

In the present work approximately 15 kg of each of the *Acacia* (W1), *Albizia* (W2) and *Leucaena* (W3) tree trunks were procured from Varanasi, India. The wood blocks measuring

approximately $6 \times 6 \times 6 \text{ cm}^3$ were sun-dried for one month and stored in vacuum desiccators. Wood cubes measuring $20 \times 20 \times 20 \text{ mm}^3$ were cut and carbonized. Six such wood cubes were placed in a mild steel crucible with a mild steel cover having 6 cm diameter and 11 cm height (Figure 3.1a). The carbonization was carried out at 600, 800 and 1100 °C for one hour in an electric muffle furnace. Slow (5 °C/min) and fast (50 °C /min) heating rates were selected to study the charcoal properties. After one hour of carbonization treatment, the crucible was placed into a vacuum oven for cooling to avoid the charcoal's air-burning. One of the wood cubes and the charcoal are shown in Figure 3.1b.

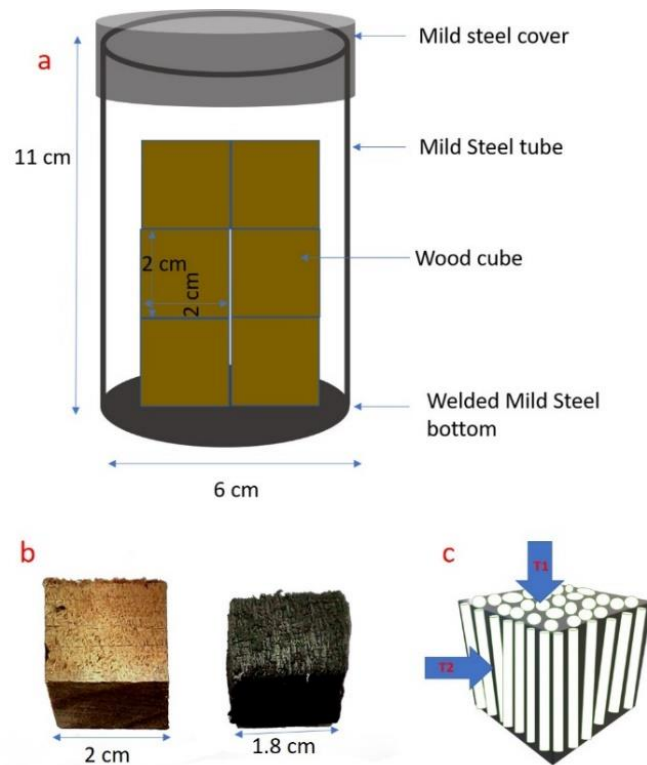


Figure 3.1 (a) Schematic diagram of the carbonization vessel, (b) a picture of dried wood and the respective charcoal sample and (c) schematic of a charcoal cube showing compressive loading directions.

3.2.2 Characterization of charcoals

Charcoal samples thus produced were weighed for calculation of charcoal yield and its dimensions were measured for calculation of volume shrinkage. Yield is defined as the ratio of the weight of charcoal produced to the weight of the initial uncarbonized biomass (Equation 3.1).

$$Yield(\%) = \left(\frac{W_c}{W_b} \right) \times 100 \quad (3.1)$$

where, W_c is weight of charcoal and W_b is weight of biomass on dried basis. Shrinkage was calculated as change in volume (from biomass cube to charcoal cube) to initial biomass cube volume.

Some of the charcoal cubes were ground to -0.05 mm (British standard 72 mesh) to perform proximate and ultimate analysis. **Proximate analysis** of different charcoals was performed using electric resistance-heated muffle type furnace as per ASTM standards, viz E872 for volatile matter, D1102 for ash content, E871 for moisture, and the fixed carbon was calculated by the difference [139].

Ultimate analysis (CHNS test) was performed by using EURO EA 3000 elemental analyzer (Eurovector, Italy) at IIT (BHU) Varanasi, India. The method for the determination of total carbon, nitrogen and hydrogen in solid biomass fuels were used as per ASTM standards, viz E777 for carbon and hydrogen, E775 for sulphur, E778 for nitrogen, and the oxygen was calculated by the difference [139]. Each test was performed thrice and average value is reported in the plots.

Compressive strength measurements were performed in two mutually perpendicular direction (Figure 3.1c) using a screw-driven Instron UTM (model 4206, at a strain rate of 0.1 mm/min) with a load of 100 kN according to the ASTM E382 [139]. **Scanning electron microscopy** (SEM; Zeiss EVO 18, Carl Zeiss, Germany) was used to study the morphology of the porous charcoal using secondary electron imaging under high vacuum mode. Pore size and area in charcoal samples were calculated from SEM images using ImageJ software. Measurements were taken at four different positions on over 100 pores in each charcoal species. Pore dimensions at a resolution of 5000× were measured for each char species and their average was taken as the pore size. The contour of the pores was marked for calculating the pore area.

Standard deviation was obtained by the square root of the sum of squared differences from the mean divided by the number of the measurements.

Fourier transform infrared (FTIR) spectroscopy was performed on charcoal powders by making KBr pellets, using Nicolet iS5 (THERMO Electron Scientific Instruments LLC) in the wavenumber range of 4000-500 cm^{-1} with a resolution of 4 cm^{-1} at 32 scans per sample. FTIR was used to obtain infrared spectrum of transmission to detect different functional groups.

Raman spectroscopy was performed in the range of 3000 and 500 cm^{-1} using an HR800-UV confocal micro-Raman spectrometer (Horiba Jobin Yvon, France) coupled to an Olympus BX41 microscope with a confocal collection system. An excitation laser of 532 nm wavelength operated at 50 mW was used. Each spectrum was analyzed between 1800 and 1000 cm^{-1} . The intensity values of the peaks at around 1350 and 1590 cm^{-1} were used to calculate intensity ratios. Raman spectra were deconvoluted into two gaussian bands, i.e., D band at 1350 cm^{-1} , G band at 1590 cm^{-1} using deconvolution application in Origin software by OriginLab (Northampton, USA).

Charcoal reactivity was evaluated against CO_2 by using a Thermo-Gravimetric (TG) type setup shown schematically in Figure 3.2. After a pre-set temperature in the vertical tube furnace was attained, a single charcoal cube loaded in the platinum basket and kept away from the heating zone at the bottom of the transparent quartz tube. Nitrogen was purged for 5 mins at a rate of 1 L/min to flush out air inside the quartz tube. The purging gas was then switched to CO_2 at the required flow rate. The basket with the charcoal cube, inside the quartz tube was then moved to the heating zone of the furnace. Weight of the Pt-basket containing the pellet was first recorded just after reaching inside the heating zone. The weight was then subsequently recorded at interval of 2 minute till completion of the reaction. After completion of the reaction, the platinum basket was lowered at the bottom end of the quartz tube. The same procedure was

precisely followed in each experiment. Charcoal reactivity (R) was calculated as per Equation 3.2.

$$\text{Reactivity (R)} = \frac{1}{W_0} \frac{dW}{dt} \quad (\text{mg} \cdot \text{min}^{-1} \cdot \text{mg}^{-1}) \quad (3.2)$$

where, W_0 and dW/dt are the initial weight and change in charcoal weight with time during reaction.

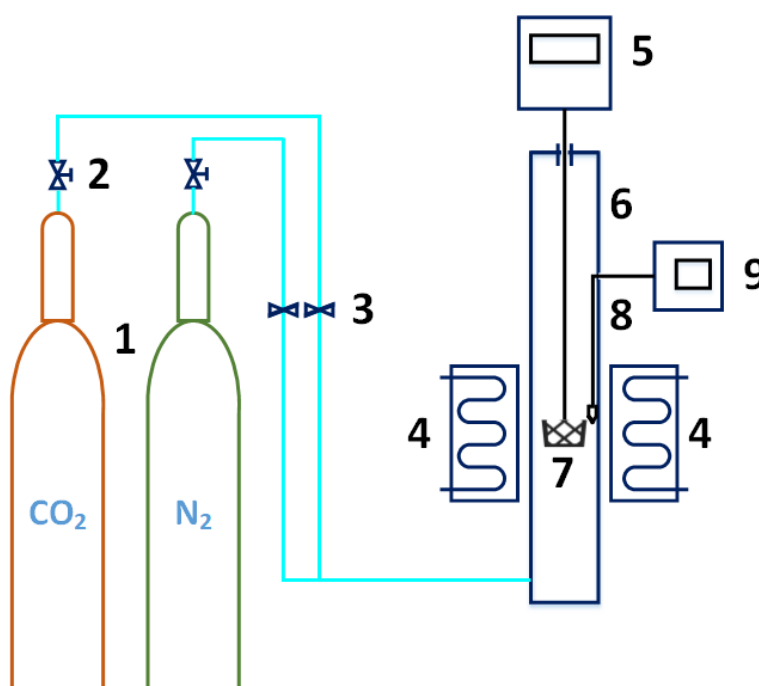


Figure 3.2: Schematic of the experimental setup employed for CO₂ reactivity tests. The components of the setup are: 1. CO₂ and N₂ Gas cylinders, 2. Gas regulator, 3. Gas flowmeter, 4. Cylindrical resistance furnace, 5. Weighing scale, 6. Quartz tube with ID: 44mm, 7. Platinum wire with Platinum basket, 8. Thermocouple, 9. PID controller.

3.3 Results and Discussion

3.3.1 Proximate analysis

Figure 3.3a shows the values of proximate analysis parameters for W1, W2 and W3 wood and respective charcoals. Change in the fixed carbon (FC) and volatile matter (VM) is higher in W1 and W2 than W3. Change in the ash content is lower in W1 and W2 than W3, suggesting higher ash content in the W3 charcoal. The composition with respect to the FC, VM and the ash content of different charcoal samples, metallurgical coke [140-142] and non-coking coals

[143, 144] is shown in a ternary diagram in Figure 3.3b. It shows that each of the wood charcoal produced has higher fixed carbon, lower ash and volatile matter content as compared with non-coking coal. It is evident from the Figure 3.3b that produced charcoals have at most 2.5% (except for W3 charcoal, which has up to 9%) ash content which is significantly lower than coals. Fixed carbon increased and the volatile matter decreased with an increase in the carbonization temperature [90, 126, 130]. At each carbonization temperature and heating rate, fixed carbon and the VM for W1 and W2 are almost equal. At any given carbonization condition, W3 has lower FC than W1 or W2. The plot shows that produced charcoals have higher (up to 10%) fixed carbon, lower (up to 10%) ash content and higher (up to 15%) volatile matter than metallurgical coke. The charcoals have higher fixed carbon, lower ash content and lower volatile matter than non-coking coal. Fast heating to carbonization temperature generally yielded charcoals with lower fixed carbon and higher volatile matter except for W3 charcoal [130].

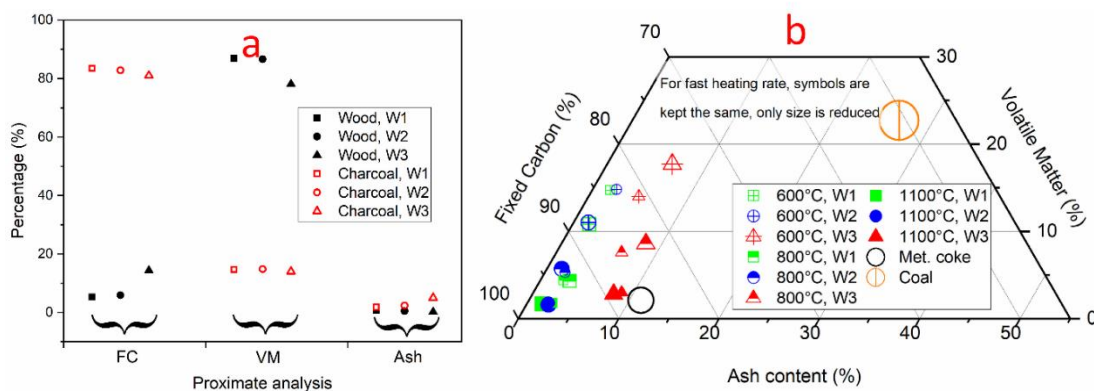


Figure 3.3 (a) Points showing FC, VM and Ash values in going from wood to charcoal at 600 °C carbonization temperature in fast heating condition and (b) a ternary diagram showing the parameters from the proximate analysis of the charcoals.

3.3.2 Ultimate analysis

Figure 3.4a shows the values of ultimate analysis parameters for W1, W2 and W3 wood and respective charcoals. Change in the total carbon content is higher in W1 and W2 than W3. The elemental composition with respect to the carbon, hydrogen and nitrogen of different charcoal

samples is shown in a ternary diagram in Figure 3.4b. It also compares ultimate analysis values among the charcoals, non-coking coal and metallurgical coke. Figure 3.4b also shows that total carbon increases with an increase in carbonization temperature. All of the charcoals have almost same hydrogen content of approximately 1-3%. The percentage of hydrogen decreases with an increase in the carbonization temperature. Produced charcoals have on average similar elemental composition and some even have higher (up to 6%) carbon and (up to 1.3%) hydrogen content compared to metallurgical coke. Charcoals have lower hydrogen and very high carbon content than non-coking coal. Fast heating rate during the carbonization led to lower total carbon in the charcoals than carbon produced with the slow heating rate. Carbon percentages in W1 and W2 are almost equal and lower in W3. Fast heating and slow heating programs for carbonization seldom affect hydrogen levels. Level of nitrogen has dropped approximately 10% after carbonization and reached almost zero in each charcoal.

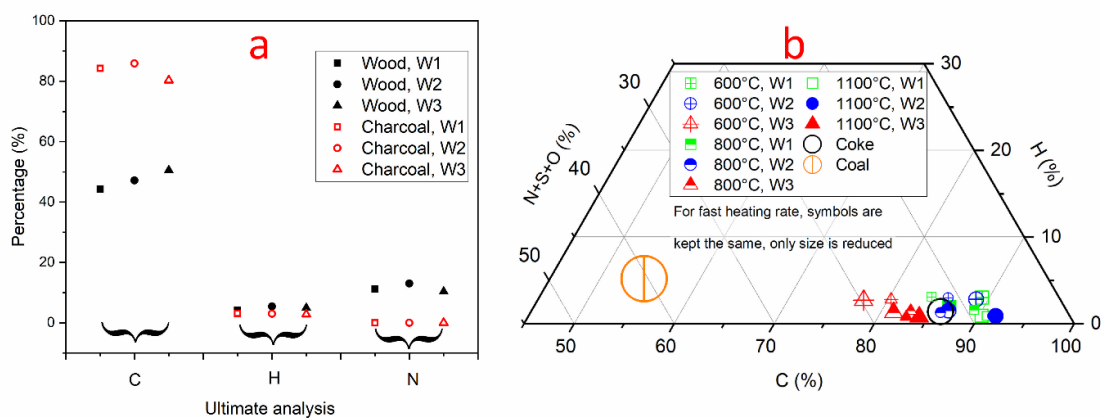


Figure 3.4 a) Points showing C, H and N values in wood and charcoal at 600 °C carbonization temperature in fast heating condition and b) Ternary diagram showing ultimate analysis values.

3.3.3 Van Krevelen diagram

The modified van Krevelen diagram [145] in Figure 3.5, classifies the solid fuels by O/C and H/C ratio. This diagram helps grade different fuels by fuel value or energy they possess. The diagram uses the fact that the C-C bond contains higher energy than C-O and C-H bonds. The

lower the value of H/C and O/C, the higher the extent of carbonization and the energy content of the fuel. We can clearly see from Figure 3.5 that wood charcoals produced in the present study have the highest carbon/energy content compared to other solid fuels. Also, it is worth noting that on average, wood charcoals produced have fuel value almost equal to metallurgical coke, which is an indispensable reductant in the blast furnace ironmaking. Fuel value increases with carbonization temperature. Also, charcoals produced at a fast-heating rate generally have a higher fuel value than those produced at slow heating. Among selected wood species, W1 and W2 charcoals have higher fuel value than W3 charcoal.

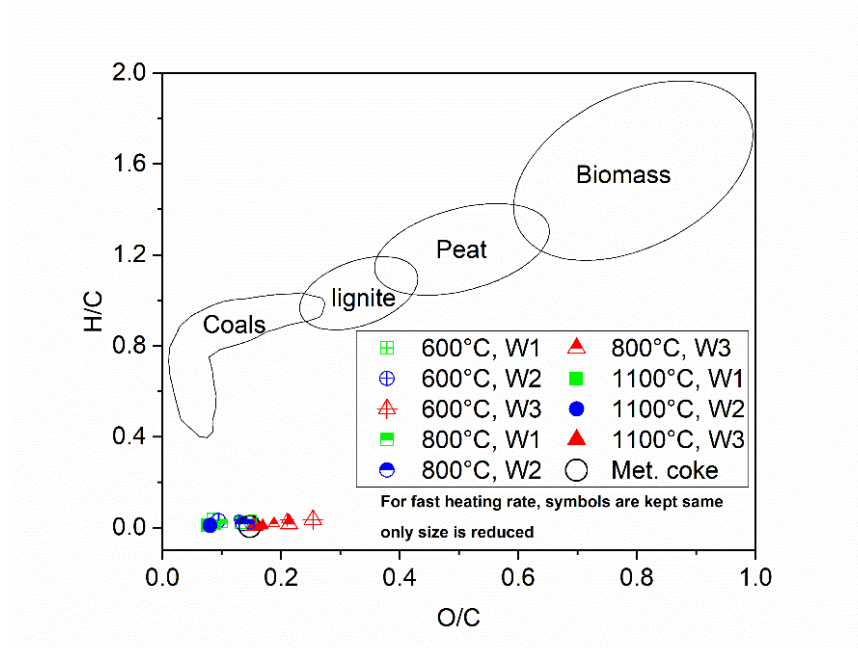


Figure 3.5 Modified van Krevelen diagram with charcoals and metallurgical coke values.

3.3.4 Charcoal yield

The charcoal yield of W1, W2 and W3 charcoals at carbonization temperatures of 600, 800 and 1100 °C, are plotted in Figure 3.6. Figure 3.6a shows that the yield of charcoal produced from biomasses in slow heating conditions decreases by 3.5, 14 and 15% for W3, W1 and W2, respectively, from a carbonization temperature of 600 to 1100 °C. Figure 3.6b shows that in

going from a carbonization temperature of 600 to 1100 °C, the yield of charcoal produced from biomasses in fast heating conditions decreases by 12, 18 and 19% for W2, W3 and W1, respectively. Various researchers [90, 126, 127, 146-148] also reported decrease in yield with increase in carbonization temperature. This decrease is due to the greater degree of gasification possible at a fast-heating rate.

Figure 3.6a and Figure 3.6b show that charcoal produced at slow heating rate has a slightly higher yield than fast heating at all selected carbonization temperatures [90, 129, 147, 148]. Among selected biomass species W3 has the highest and W2 the lowest yield at all carbonization temperatures i.e., 600, 800 and 1100 °C.

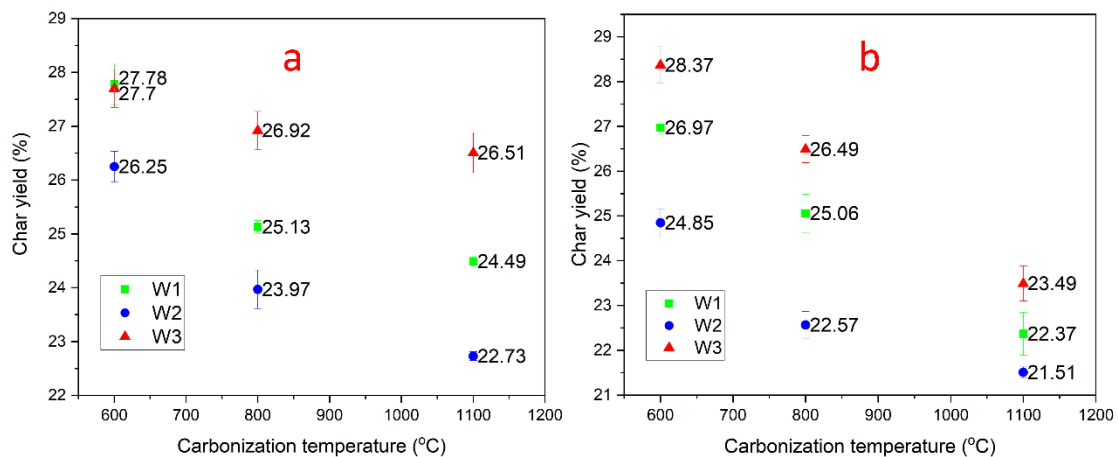


Figure 3.6 Variation of charcoal yield with carbonization temperature for different biomasses in a) slow heating b) fast heating condition.

3.3.5 Volume shrinkage

Volume shrinkage values at carbonization temperatures of 600, 800 and 1100 °C for W1, W2 and W3 during slow and fast heating conditions are plotted in Figure 3.7. Figure 3.7a shows that the volume shrinkage increases by 16, 28 and 24% with a rise in temperature from 600 to 1100 °C in slow heating conditions for W1, W2 and W3, respectively. Figure 3.7b shows that with a rise in the carbonization temperature from 600 to 1100 °C, volume shrinkage of charcoal produced from biomasses in fast heating conditions increases by 29, 10 and 12% for W1, W2

and W3, respectively. Figure 3.7a and Figure 3.7b also show that charcoals produced at slow heating has higher volume shrinkage than fast heating at all selected carbonization temperatures. Volume shrinkage during carbonization increases with an increase in temperature and decrease in heating rate [149-152]. Among selected biomass species W2 (59%) has the highest and W3 (51%) has the lowest volume shrinkage at all carbonization temperatures i.e., 600, 800 and 1100 °C.

Paris et al. [97] identified three distinct temperature regions during the carbonization of biomass. The first region is 25-247 °C, where dehydration along with slight depolymerization and evaporation of water is noticed. The second region is 247-347 °C, where major degradation of all biopolymers and evaporation of low-molecular-weight fragments take place leading to substantial dimensional change and mass loss. The crystal structure of cellulose fully degenerates and the microstructure appears completely disintegrated and fully random. The third region is above 347 °C, where the presence of polyaromatic compounds were noticed for the first time. Beginning stacking of two-dimensional ordered graphene sheets indicated turbostratic carbon formation and progressive ordering [153]. Up to 1027 °C, the average number of stacked carbon sheets remains constant, while their amount and in-plane dimensions increase continuously. They also found that a slightly preferred orientation of the carbon sheets parallel to the cell axis developed again above 427 °C, which improved with temperature.

Up to 600 °C, hemicellulose and cellulose are already dissociated, leaving only lignin to dissociate as temperature increases further [97, 154, 155]. Lignin dissociation (160-900 °C) forms turbostratic carbon lowering the yield and increasing the shrinkage in the matrix. The lower level of fixed and total carbon, higher yield and lower shrinkage in W3 than W1 and W2 can be attributed to lower lignin content in W3 wood [90, 156-158]. Volume shrinkage occurs in the matrix due to the dissociation of wood components to form charcoal. In the case of fast

heating, less time is available for dissociation reactions to occur and hence lower is the volume shrinkage.

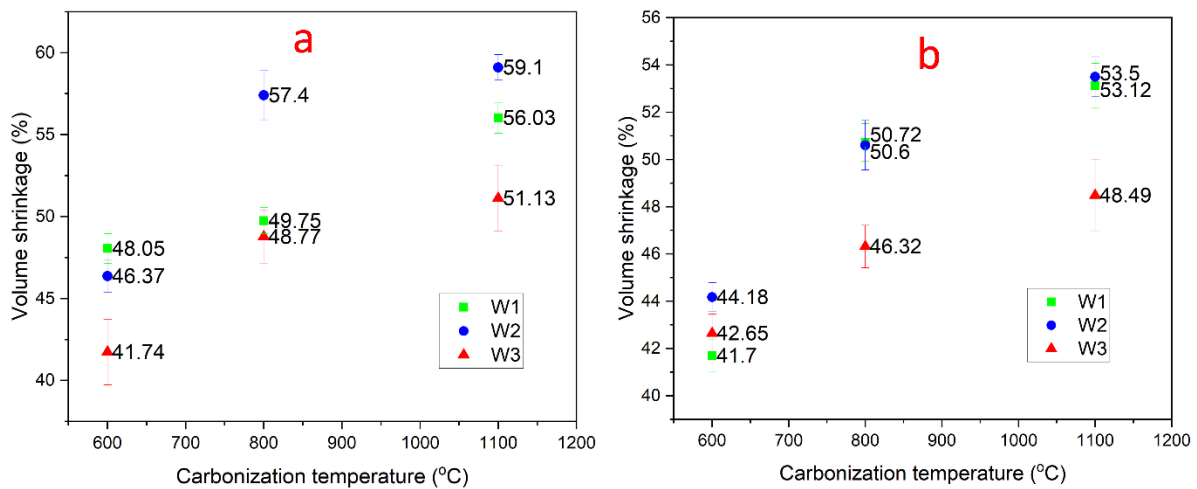


Figure 3.7 Variation of charcoal volume shrinkage with carbonization temperature for different biomasses in a) slow and b) fast heating condition.

3.3.6 Compressive strength

Compressive strength is a measure of the maximum weight of the overburden that charcoals can endure. Compressive strength values in T1 (longitudinal) and T2 (tangential) directions at carbonization temperatures of 600, 800 and 1100 °C for W1, W2 and W3 charcoals during slow and fast heating conditions are plotted in Figure 3.8. Compressive strength is higher in the T1 direction (2-10 MPa) than the T2 direction (0.8-7 MPa) at a fixed carbonization temperature in selected wood charcoals. Compressive strength of charcoals produced at fast and slow heating rates generally increases from 0.8-10 MPa with increase in carbonization temperature for all the wood species in both loading directions under fast and slow heating rates. Compressive strength for charcoals produced at the slow heating (0.9-10 MPa) rate is higher than the strength of the charcoals produced at fast heating (0.8-6 MPa) rate for each wood species in either loading directions. W1 (2-10 MPa) and W2 (1-8 MPa) charcoals generally have higher compressive strength than W3 (0.8-7 MPa) at different carbonization temperatures at both heating rates and loading directions. It is worth noting that after carbonization at 1100 °C at the fast-heating rate, W1 and W3 wood charcoals disintegrated in

two or more pieces while W2 charcoal stayed as a monolithic charcoal cube. During the carbonization of biomasses, the evolution of volatile matter leads to a highly porous matrix that consolidates and gives rise to shrinkage. At the fast-heating rate the wood is suddenly exposed to the carbonization temperature of 1100 °C from the ambient temperature resulting in a very high rate of volatile matter evolution, disrupting the integrity of the transient structure. Thus, carbonization at 1100 °C at a fast-heating rate is offering no advantage concerning the strength of the charcoal. An optimum carbonization temperature could exist somewhere between 800 and 1100 °C for the wood species of W2 and W3. An attempt at to explain these phenomena has been attempted in the next section with the aid of SEM micrographs.

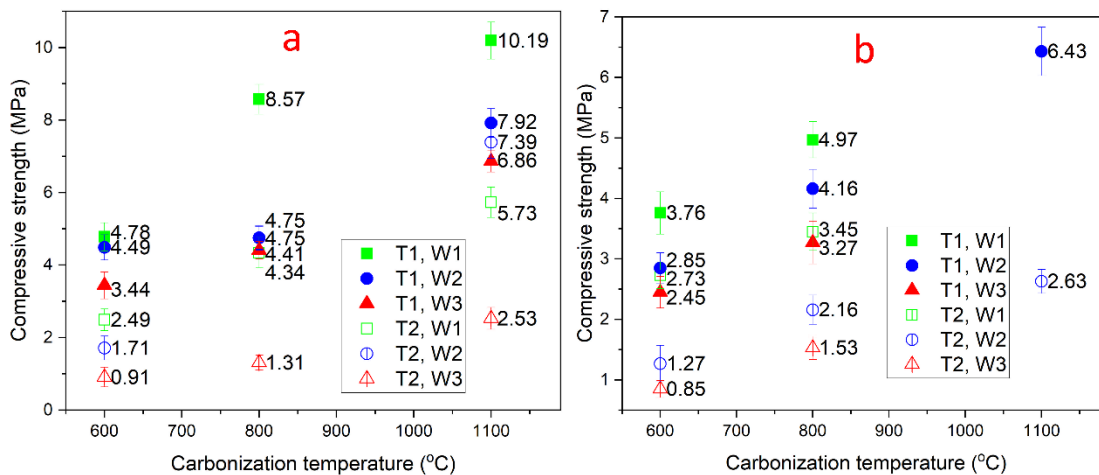


Figure 3.8 Variation of compressive strength with carbonization temperature for different biomasses in a) slow and b) fast heating condition.

3.3.7 SEM analysis

Figure 3.9a shows the SEM images of W3 charcoals produced at different carbonization temperature and heating rates. Carbonization time was fixed for one hour. Figure 3.9b shows the microstructures of the charcoals of different species produced at the fast-heating rate at the carbonization temperature of 1100 °C to compare the pore morphologies across different wood species. As evident from Figure 3.9a, charcoals produced at faster heating generally have bigger pores and thinner pore walls, which might be the reason for their lower strength. W1

has thicker pore walls which provide support and higher compressive strength under load. However, having smaller pores reduces the surface area available for iron ore reduction and CO₂ gasification using charcoal (Figure 3.9b).

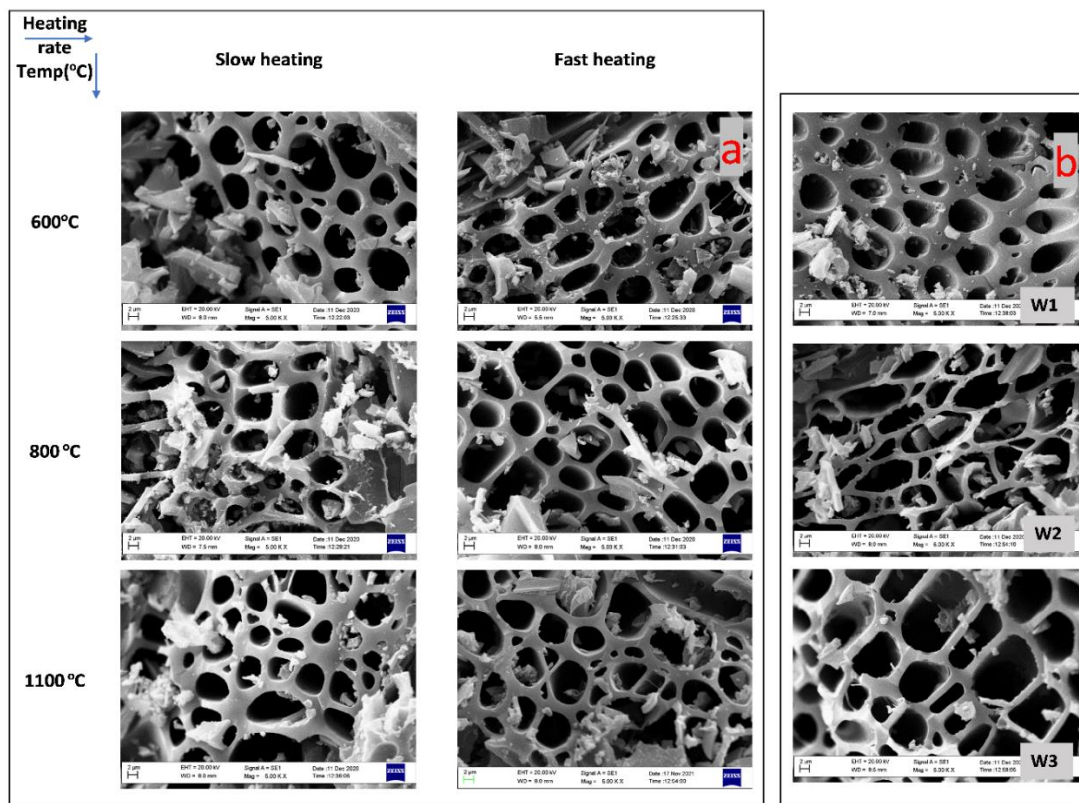


Figure 3.9 SEM images of a) W3 charcoals produced at different carbonization temperature and heating rate at 1-hour soaking time, b) different charcoals produced at 1100 °C in fast heating at 1hour soaking time.

Table 3.1 shows pore sizes and intrapore distance for charcoal of different species at 5000 \times . Pore and intrapore spaces do not present a valuable and definite picture (Table 3.1). Closer values and higher standard deviation is due to irregular and non-uniform pore structure. For better quantification of irregular pores, pore areas were calculated. Average pore area values (Table 3.1) show that W2 (43 μm^2) and W3 (58 μm^2) charcoals have bigger pores than W1 (36 μm^2). This could also mean more open surface area for the reduction and gasification process, making them better reductant and fuel. During fast heating for carbonization, W3 charcoal yields charcoals with higher fixed carbon and lower volatile matter as opposed to the trend followed by W1 and W2 charcoals. W3 possibly behaves differently because of its relatively

larger pores which let the volatile matters escape even at fast heating rates. Larger pores of W3 charcoal than W1 and W2 charcoal might also be the reason for the lower compressive strength of W3 charcoal than W1 and W2. Pore geometries are noticed to be round, oval and rectangular for W1, W2 and W3, respectively.

Table 3.1 Pore and intrapore sizes for charcoals shown in Figure 3.9b.

| Wood type | Pore size (μm) | Intrapore space (μm) | Pore area (μm^2) |
|-----------|-----------------------------|-----------------------------------|-------------------------------|
| W1 | 7.14 \pm 1.46 | 1.87 \pm 0.37 | 36.34 \pm 3.41 |
| W2 | 8.15 \pm 1.44 | 1.04 \pm 0.20 | 42.91 \pm 5.09 |
| W3 | 7.69 \pm 1.18 | 1.82 \pm 0.32 | 57.73 \pm 7.32 |

3.3.8 Fourier transform infrared spectroscopy

Figure 3.10a, b and c show FT-IR spectra at different temperatures for W1, W2 and W3 charcoals, respectively. In Figure 3.10, peaks at 2100, 1990, 1577, 875 and 747 cm^{-1} are present, corresponding to alkyne, allene, alkene and C-H bending in unsaturated hydrocarbons, respectively [159, 160]. Weak peak intensity of each functional group in the diagnostic region (3500-1600 cm^{-1}) indicates a small amount (per unit volume) of groups associated with the molecular bond. Most of these bands disappear with a rise in carbonization temperature up to 1100 $^{\circ}\text{C}$ except for ones at 2100, 1990 and 747 cm^{-1} . In W1 and W2 charcoals (Figure 3.10a and b), at 600 $^{\circ}\text{C}$, a band is present at 1160 cm^{-1} in addition to common bands mentioned above corresponding to C-O stretching in tertiary alcohol which disappears with a further rise in temperature. A weak band at 1690 cm^{-1} is present in W2 charcoal (Figure 3.10b) carbonized at 600 $^{\circ}\text{C}$, corresponding to the ketone group, which also disappears with temperature rise.

Similarly, a band is present in W3 charcoal (Figure 3.10c) at 600 °C at 1410 cm^{-1} , corresponding to O-H bending in alcohol or carboxylic acid [161]. The absorption band at 1577 cm^{-1} can be attributed to C=C stretching vibrations in aromatic compounds. The bands located at 875 and 747 cm^{-1} indicate C-H out-of-plane bending in an aromatic ring. These bands are present in the charcoals at 600 °C and disappear above 800 °C, indicating that macromolecular aromatic molecules began to rearrange at this temperature [162]. Lignin constitutes of 3 monolignols that are coumaryl alcohol, coniferyl alcohol and sinapyl alcohol [163] and disappearance of bands corresponding to alcohol, ketone and unsaturated hydrocarbons group at 1920, 1690, 1577 and 1410 cm^{-1} suggests degradation of lignin to form disordered/turbostratic carbon at temperatures excess to 800 °C [164].

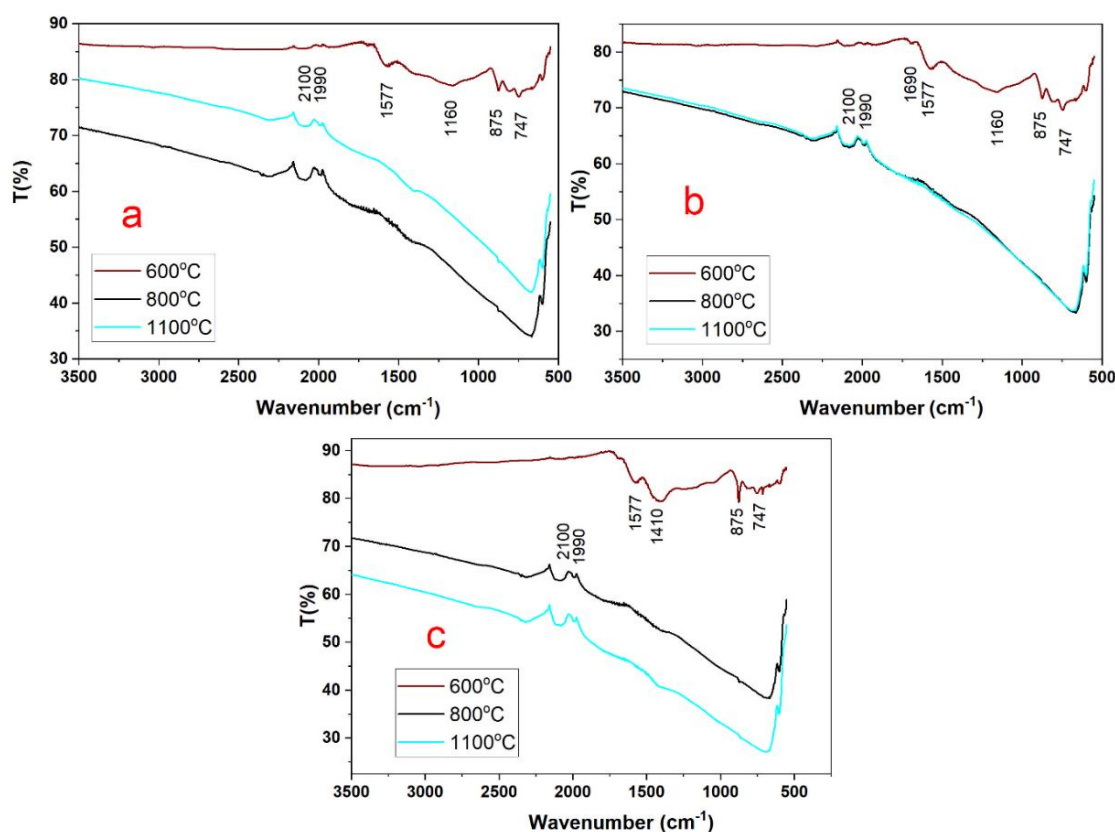


Figure 3.10 FT-IR spectra for a) W1, b) W2. C) W3 Charcoals at different temperature.

3.3.9 Raman spectroscopy

Raman spectra at different temperatures for W1, W2 and W3 charcoals are shown Figure 3.11a, b and c, respectively. In Figure 3.11, two peaks can be noticed around 1350 and 1580 cm^{-1} . Peak around 1580 cm^{-1} is referred to as graphite or G band is characteristic of sp^2 carbon present. In disordered and distorted graphitic structures like turbostratic carbon, one additional peak is observed at 1350 cm^{-1} referred to as defect or D band [97].

Table 3.2 contains characteristics of deconvoluted Raman spectra peaks. D band is located at 1360, 1368 and 1375 cm^{-1} in W1, W2 and W3, respectively (Table 3.2). G band is located at 1595, 1590 and 1590 cm^{-1} in W1, W2 and W3, respectively. In addition to D and G band, S band is also present in W2 charcoal (Figure 3.11b) at 1100 cm^{-1} [165, 166]. The ratio of the intensities of D band to G band is 0.622, 0.688 and 0.841 for W1, W2 and W3, respectively. The ratio of area covered by D band to G band is 1.79, 1.95 and 3.63 for W1, W2 and W3, respectively. FWHM increases for D and G band from W1, W2 and W3 (Table 3.2).

Overlapping D and G bands are seen in Raman spectra (Figure 3.11) due to the high proportion of amorphous carbon. With the decrease in the ordering of carbon, D band shifts towards higher and G band towards the lower wavenumber [167]. The amount of the shift in peak position indicates the proportion of disordered carbon. S band is characteristic to sp^3 hybridized carbon, which may be due presence of allylic and benzylic carbon in W2 charcoal. Higher intensity and area of D band mean a higher disorder in the material. Higher I_D/I_G and A_D/A_G indicate a higher proportion of large aromatic clusters [167]. Sharp Raman peaks are observed in crystalline materials, which means that full width at half maxima will increase with the increasing disorder in material [108]. Peak position shift, I_D/I_G , A_D/A_G , and FWHM values in Raman spectra combinedly suggest that W3 char has the highest amount of disordered/turbostratic carbon and W1 has the lowest among selected charcoals. Materials with

higher disorder or open structures have higher reactivity, leading to higher gasification and, hence, a greater extent of iron ore reduction.

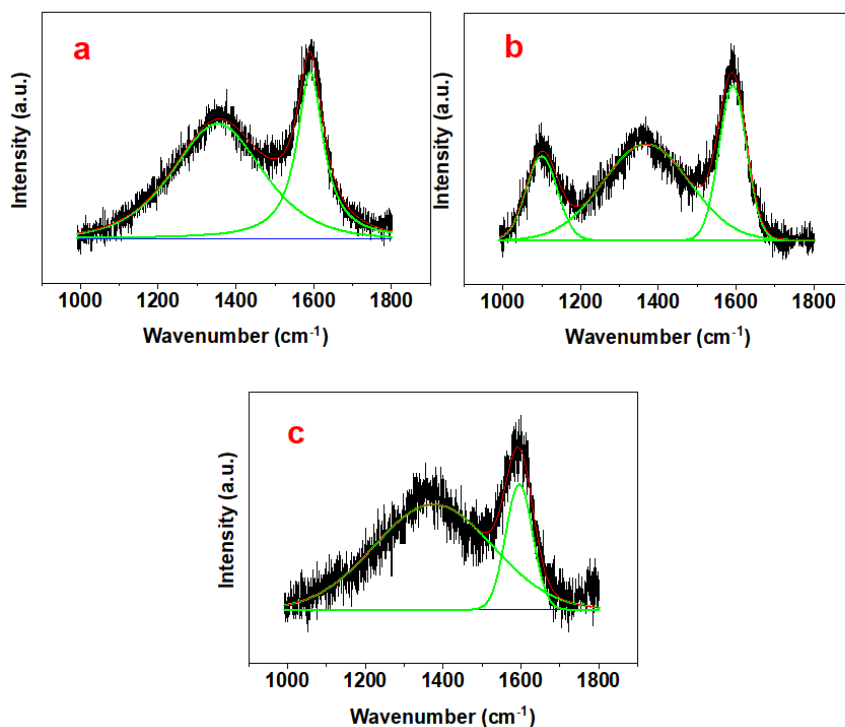


Figure 3.11 Raman spectra of a) W1, b) W2. C) W3 charcoals.

Table 3.2 Deconvoluted Raman spectra peak characteristics.

| Char | Band | Peak position (cm ⁻¹) | FWHM | I _D /I _G | A _D /A _G |
|------|------|-----------------------------------|---------------|--------------------------------|--------------------------------|
| W1 | D | 1360(±4) | 263.21(±4.51) | 0.622(±0.05) | 1.79(±0.06) |
| | G | 1595(±5) | 81.89(±3.02) | | |
| W2 | S | 1100(±3) | 95.01(±2.05) | 0.688(±0.06) | 1.95(±0.07) |
| | D | 1368(±6) | 270.40(±6.17) | | |
| | G | 1590(±4) | 83.79(±3.96) | | |
| W3 | D | 1375(±6) | 357.66(±9.28) | 0.841(±0.05) | 3.63(±0.08) |

| | | | | | |
|--|---|----------|--------------|--|--|
| | G | 1590(±5) | 86.01(±4.46) | | |
|--|---|----------|--------------|--|--|

3.3.10 Charcoal reactivity

Carbon gasification or Boudouard reaction, i.e., $C+CO_2 \rightarrow 2CO$ is the rate limiting step in iron ore reduction process. The carbon reactivity is the measure of the rate at which carbon is able to react to get converted into CO gas. Knowledge of the reactivity of different charcoals will help choose better reductant.

To avoid situations like CO₂ gas starvation and wastage during further experiments, gas flow rate was optimized. Reactivity of the charcoal increases with increase in gas flow rate from 0.4 to 0.6 L/min (Table 3.3). The increase in reactivity of the charcoal is a result of improved gas availability with the increased gas flow rate. At flow rates greater than 0.6 L/min, reactivity decreases slightly, indicating no further use for increased gas flow towards the gasification reaction. Hence, the flow rate of 0.6 L/min was taken as optimum for further experiments.

Table 3.3 Variation of reactivity with CO₂ gas flow rate at reactivity temp of 950°C with W3 charcoal carbonized at 600 °C

| | | | | |
|--|------|------|------|------|
| CO ₂ gas flow (L/min) | 0.4 | 0.6 | 0.8 | 1 |
| R×10 ³ (mg min ⁻¹ mg ⁻¹) | 20.4 | 45.1 | 43.7 | 43.9 |

Variation in reactivity of charcoals with reactivity temperature is presented in Table 3.4. It is apparent from the results that reactivity increases monotonically with increase in the reaction temperature. It is noticeable that W1 and W2 species have a big jump in reactivity values at temperatures in excess of 900 °C. At reactivity temperature of 1000 °C, reactivities of W1 and W3 species reach 62 and 83 min⁻¹ respectively. However, the effect of reactivity temperature is rather small in case of W3 species, exhibiting the peak reactivity of 59 min⁻¹. This could possibly be due to high initial porosity in W3 charcoals whereas porosity improves with rise in reactivity temperature in case of W1 and W2.

Table 3.4 Variation of charcoal reactivity with reactivity temperature, for charcoals prepared at 600 °C

| Charcoal | W1 | | | | W2 | | | | W3 | | | |
|---|------|------|------|------|------|------|------|------|------|------|-----|------|
| | 850 | 900 | 950 | 1000 | 850 | 900 | 950 | 1000 | 850 | 900 | 950 | 1000 |
| R×10 ³ (mg min ⁻¹ mg ⁻¹) | 17.5 | 44.7 | 45.1 | 62.2 | 18.2 | 45.3 | 61.9 | 83 | 25.7 | 45.9 | 53 | 58.5 |

Variation in reactivity of charcoals with charcoal species is presented in Table 3.5. Results suggest that charcoal reactivity is a function of both reactivity temperature and charcoal species. At reactivity temperatures of 800 and 900 °C, W3 is the most reactive species. However, at 950 and 1000 °C, W2 is the most reactive.

Table 3.5 Variation of reactivity with charcoal species carbonized at 600 °C

| Reactivity temp (°C) | 800 | | | 900 | | | 950 | | | 1000 | | |
|--|------|------|------|------|------|------|------|------|----|------|----|------|
| | W1 | W2 | W3 | W1 | W2 | W3 | W1 | W2 | W3 | W1 | W2 | W3 |
| R×10 ³ (mg min ⁻¹ mg ⁻¹) | 17.5 | 18.2 | 25.7 | 44.7 | 45.3 | 45.9 | 45.1 | 61.9 | 53 | 62.2 | 83 | 58.5 |

Variation in reactivity of charcoals with charcoal carbonization temperature is presented in Table 3.6. Results showed that carbonization temperature of 800 °C was found to be optimum. This could be due to increase in the content of amorphous carbon till a carbonization temperature of 800 °C. Beyond 800 °C, due possibly to increased ordering of amorphous carbon, the reactivity decreased.

Table 3.6 Variation of reactivity with carbonization temperature at reactivity temp of 950 °C

| Charcoal | W1 | | | W2 | | | W3 | | |
|--|------|------|------|------|------|------|-----|------|------|
| Carbonization Temp (°C) | 600 | 800 | 1100 | 600 | 800 | 1100 | 600 | 800 | 1100 |
| $R \times 10^3$ (mg min ⁻¹ mg ⁻¹) | 45.1 | 71.4 | 38.1 | 61.9 | 65.2 | 49.6 | 53 | 57.1 | 50.3 |

Charcoals with higher fixed carbon content, yield, porosity and disordered carbon content make better reductants for ironmaking. W1 has higher carbon content than W2 and W3 in the present study. The latter offer higher yield, porosity, disordered carbon content and charcoal reactivity towards CO₂. Higher porosity and disordered carbon content and reactivity make charcoal a better reducing agent [94]. Therefore, W2 and W3 are potentially better reductants than W1 for ironmaking via the direct reduction route.

3.4 Conclusions

In the past, charcoals have been proposed as a CO₂-neutral reductant and a source of energy. “Metallurgical” charcoals are required to have a minimum of 85% fixed carbon along with low ash and low volatile matter content [126]. At the carbonization temperature of 800 °C studied here, the *Acacia*, *Albizia* and *Leucaena* resulted in charcoal with a fixed carbon content of 93.3, 92.7 and 85.9%, respectively, each exhibiting a value above the minimum specified for the metallurgical charcoal. Further notable conclusions of this study are:

1. Overall yield for different wood species varied from 21-28%. The charcoal yield was the highest in *Leucaena*. The yield of the charcoals decreased with increase in carbonization temperature and heating rate. Porosity was highest in *Leucaena* charcoals. Due to poor strength, charcoals cannot substitute coke in blast furnace. They can be used in mini blast furnace or in alternative route of ironmaking.

2. FT-IR spectra demonstrated the degradation of lignin to form turbostratic carbon at temperatures greater than 800 °C. Raman spectra analysis suggested *Leucaena* char has the highest amount of disordered/turbostratic carbon and *Acacia* has the lowest among the charcoals studied.
3. The reactivity is higher in W2 and W3 charcoals than W1 charcoals. Charcoals carbonized at 800 °C were found to be more reactive than at 600 and 1100 °C.
4. Yield, porosity, disordered carbon content and charcoal reactivity are more important for a reductant and should take precedence over the fixed carbon content. Based on the characteristics of the selected charcoals, *Albizia* and *Leucaena* are better reductant than *Acacia* for ironmaking process.