Chapter 2 Selection and characterization of biomass species for ironmaking

In this chapter, suitable wood species were selected for their potential application in direct reduction of iron ore. The selected wood species were characterized extensively using proximate analysis, ultimate (CHNS) analysis, thermal stability test, apparent specific gravity, true specific gravity, porosity, compressive strength, nature and morphology of wood fibers (SEM microscopy) for their suitability in ironmaking.

2.1 Introduction

The steel industry is dependent on fossil fuel for its need of a reductant and energy, accounting for a maximum of 2.6 Gt CO_2 emission which is 7% of global greenhouse gas emissions [16]. The reserves of fossil fuels are limited and non-renewable in nature. According to one estimate, the coal reserves will last for approximately 139 years [11]. The use of these fossil fuels is believed to cause severe environmental problems due to CO_2 emission [111]. The alarming rise in level of CO_2 (285 ppm in 1850 [17] to 421 ppm in June, 2022 [18]) in our atmosphere needs urgent solutions to save the life on the planet [112, 113].

In coming years governments will impose strict emission norms for iron and steel industries, forcing them to use eco-friendly energy like hydrogen or renewable biomass only. The carbon from biomass appears most suitable, CO_2-neutral, renewable and sustainable energy source [114]. With over 300 sunny days in a year, Indian tropical climate is very favorable for biomass cultivation [115]. Recent reviews [116, 117] of the use of biofuels in iron and steel industries identified the high price a major obstacle. However, more recently in October 2021, the hard coking coal prices touched a record level of AUD$600/MT, making up for more than 50% of raw material cost of steelmaking

Note: Portions of this chapter have also been published in Singh AK, Mishra B, Kumar S, Sinha OP, Singh R, *Biomass Convers and Biorefin* 2022; 1-12.

in a blast furnace [118]. Rising prices of the fossil fuels and a prospect of carbon tax in near future have made the use of biomass very attractive in the iron and steel making.

A significant number of works on the use of biomass in coke making, iron ore sintering, carbon composite agglomerate, PCI, in electric arc furnace are reported in literature. In order to use biomass in iron making processes as reductant it is necessary to identify suitable biomass species that have higher potential of use. The species has to be suitable for ironmaking as well as for short rotation forestry. High calorific value, strength, density, growth rate and biomass yield are desired qualities for such biomasses [114]. Biomasses should also have high adaptability to diverse climate, soil & altitudes, resistance to pests & diseases, regenerative capacity. After imposing these parameters to agronomy data [119], hardwood species like *Acacia nilotica, Eucalyptus globulus, Albizia lebbeck, Leucaena leucocephala, Dalbergia sissoo, Prosopis cineraria* and *Casurina equisetifolia* were shortlisted as promising species under Indian climate. Among these species, *Acacia nilotica* and *Eucalyptus globulus* were characterized and carbonized by Kumar and Gupta [91, 96]. The authors however did not study the reduction of iron ore using these charcoals.

Acacia nilotica (W1) was selected for comparison with the previous work by Kumar and Gupta [91, 96]. *Albizia lebbeck* (W2) and *Leucaena leucocephala* (W3) were selected as novel species in the present study. In the next chapter selected biomasses will be used for making wood charcoal, which could be the most promising substitute for fossil coal in ironmaking. Charcoal used from selected species will be used as raw materials for producing reductant and energy source for iron making. The basic requirements for cultivating selected hardwood species are listed in Table 2.1.

Table 2.1 Geoclimatic requirements for cultivating selected hardwood species [119-121]

Wood Species	Common name in India	Babool	Siris	Subabul
	Botanical name	*Acacia Nilotica* (W1)	*Albizia Lebbeck* (W2)	*Leucaena leucocephala* (W3)
Favourable climate		Arid and semi-arid	Semi-arid to sub-humid areas of the tropics and subtropics	Sub-humid or humid
Soil requirement		Alluvial plains and Indian peninsular region	Prefers a well-drained, moisture-retentive soil	Wide range of deep well drained, fertile neutral soil. It can tolerate saline and acid soil with adequate rainfall upto 1.50 m
Annual Rainfall (m)		0.6 - 1.2	0.60 - 2.50	0.50 - 3.0
Wood density (kg/m^3)		835	660	550
Plant height (m)		> 12	≈ 25	> 15

2.2 Experimental

2.2.1 Procurement of raw materials

In the present work 15 kg of each of the W1, W2 and W3 wood samples were procured from 5 different trees of each wood species from Varanasi, India. The same were sun dried for 1 month and stored in plastic bags. Wood cube samples with an edge of 0.02 m (volume 8×10^{-6} m^3) were used to determine their specific gravities, compressive strength, SEM imaging. Sawdust from the same samples were used for proximate, ultimate and thermal stability test.

2.2.2 Characterization of biomasses

The chemical (proximate and ultimate analysis), physical (specific gravity and porosity), structural (scanning electron microscopy) and mechanical (compression test) properties of the aforementioned wood species were examined. The proximate analysis was done to determine the contents of moisture, volatile matter and ash present in biomasses. The ultimate analysis or

CHNS (carbon, hydrogen, nitrogen and sulphur) test was performed to determine the elemental composition. Thermal stability test was to understand the stability of different macromolecules with rise in temperature. Specific gravity and porosity measurements provided extent of material and pore volumes present. Compressive strength was evaluated to determine load carrying capacity of individual biomasses.

Each wood sample was crushed to -250 µm powder for performing chemical analysis and TGA. Wood cubes of 2×10^{-6} m^3 were used for porosity, compression test and morphological studies. **Proximate analysis** of different species was performed using electric resistance-heated muffle type furnace as per ASTM standards viz for moisture E871-82(2019), for volatile matter E872-82(2019), for ash content D1102-84(2021). Wood sawdust in silica dish (dia: 50 mm, depth: 10 mm) without lid was exposed to a temperature of 110±5 ℃ for 1 hour to determine moisture content. Sawdust in quartz crucible (dia: 25 mm, depth: 40 mm) with lid was exposed to a temperature of 925±5 ℃ for 7 minutes to determine volatile matter content. Sawdust in silica dish (dia: 50 mm, depth: 10 mm) without lid was exposed first to a temperature of 400±5 ℃ for 30 minutes, it was then transferred to another furnace at a temperature of 800±5 ℃ for 1 hour to determine ash content. The fixed carbon content was calculated by the difference i.e., FC% =100- (Moisture+ Volatile matter + Ash content) %. **Ultimate analysis** (i.e., CHNS test) of the same sawdust was performed by using EURO EA 3000 elemental analyzer (Eurovector, Italy) at IIT (BHU) Varanasi, India. Weighed sawdust samples (5-10 mg) were made into tin capsules and exposed to a reactor at 1000 °C for flash combustion. During flash combustion, C, H, N and S are converted to their respective stable oxides and based on amount of these gases, the detector quantifies the amount of the elements in the sawdust. Oxygen content was calculated by the difference i.e., O%= 100- (C+N+H) %. These tests were performed thrice and the average value is reported with the standard deviation. The method for the determination of total carbon, nitrogen and hydrogen in solid biomass fuels was used as per the procedure described in the European / British standard BS EN ISO 16948:2015. **Thermal stability test**

was performed in a TGA-50 by Shimadzu (Asia Pacific Pvt Ltd) according to ASTM E2550 − 21.

Apparent specific gravity of cubic wood samples was determined by hot boiling water method as per the specifications ASTM C20 – 00 (2022) using Equation 2.1.

$$\text{Apparent specific gravity} = \frac{D}{(D-S)} \qquad (2.1)$$

where, D is the dry weight of wood sample and S is the suspended weight of wood sample in water.

True specific gravity of wood sawdust was measured by using the specific gravity bottle method, as per the specification BIS IS 1122:1974(R2003) using Equation 2.2.

$$\text{True specific gravity} = \frac{(w_2 - w_1)}{(w_4 - w_1) - (w_3 - w_2)} \qquad (2.2)$$

where,

w_1: weight of empty bottle with stopper

w_2: weight of bottle with powder and stopper

w_3: weight of bottle with powder, fluid and stopper

w_4: weight of bottle with fluid and stopper

The total porosity was calculated from the apparent sp. gravity and true sp. gravity values using Equation 2.3.

$$\text{Total porosity } (\%) = \left(1 - \frac{\text{Apparent specific gravity}}{\text{True specific gravity}}\right) \times 100 \qquad (2.3)$$

The compressive strength was evaluated by compression test performed on a cubical 2×2×2 cm^3 wood sample along the three mutually perpendicular loading directions. The longitudinal plane loading is denoted as "T1" and the two transverse plane loading are denoted as "T2" and "T3" respectively as shown in Figure 2.1.

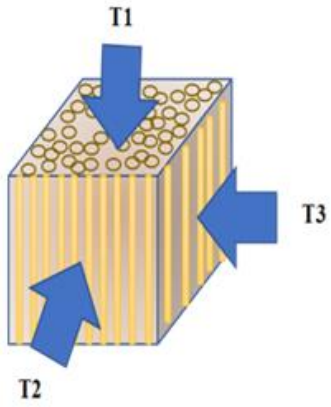

Figure 2.1 Schematic wood cube showing three mutually perpendicular loading directions for compression test.

Pores and surface characteristics of biomass are important for fuel and reductant and were examined using the **scanning electron microscopy (SEM)**. A scanning electron microscope (model ZEISS EVO-18, Oxford Instruments with software INCA Energy 300, acceleration voltage = 20 kV, and beam current ≈ 5 mA) coupled with EDS (51N1000 – EDS System, Oxford Instruments Nanoanalysis) was used to study biomasses. SEM was performed after gold coating the sample. Bulk wood samples were used to get micrographs with pore morphology. Pore size in wood samples were calculated from SEM images using ImageJ software from the National Institute of Health and the Laboratory for Optical and Computational Instrumentation (LOCI, University of Wisconsin, USA). Measurements were taken at four different positions on over 100 pores in each wood species. Pores in an image at 5000× were measured for each wood species and their average was taken as the pore size. Standard deviation was obtained by the square root of the sum of squared differences from the mean divided by the number of the measurements.

2.3 Results and discussion

2.3.1 Proximate analysis

Proximate analysis values for each wood species (i.e., W1, W2 and W3) are shown in Figure 2.2. All the values mentioned are in weight% unless otherwise stated. It is evident from the Figure 2.2 that moisture content is practically the same (7%) in all the species. The ash contents in the studied biomasses were reasonably low. Among the three wood species, W1 had the highest and W3 had the lowest ash content. The percentage of volatile matter was almost the same for W1 and W2 (≈ 72%), however, W3 had the lowest volatile content (64%) among all the three biomasses. W3 had the highest fixed carbon content of 28.8%, whereas W1 and W2 had 20.5% and 19.9% respectively. Fixed carbon is defined as a measure of the amount of non-volatile carbon remaining in a coal/charcoal sample.

Biomasses exhibit a wide range of composition. Earlier work on different biomasses indicated that the hardwood variety which could be used for direct reduction of iron ore contained 65-83% VM and 40-54% total carbon on air dried basis [91, 104, 122, 123]. The respective values in this study (VM: 64-73% & total C: 44-51%) fell in the range reported in literature. Being fast-growing biomasses, the selected species are preferable over others. Volatile matter and carbon in the wood actively take part in the reduction of iron ore pellets and hence these parameters from the proximate analysis of the wood influence its efficacy in DRI making. Proximate analysis values at best inform about the compounds in the biomass. Ultimate analysis was performed, assaying further the elements present in those compounds.

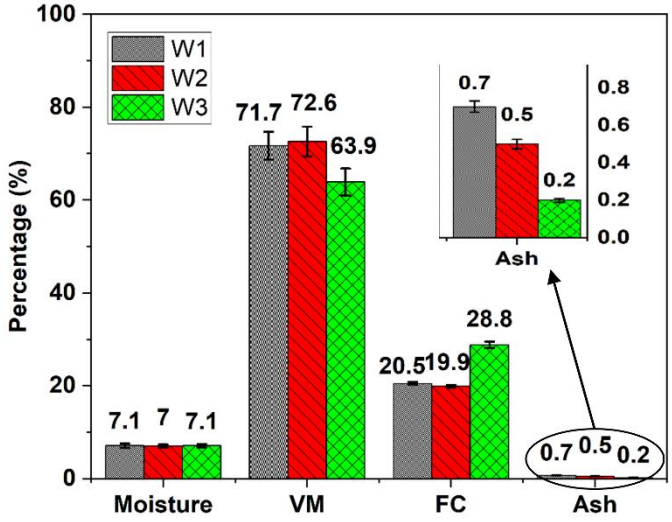

Figure 2.2 Proximate values of biomass.

2.3.2 Ultimate analysis

The results of ultimate analysis values for different woods are shown in Figure 2.3. Hydrogen content was the highest in W2 and the lowest in W1 wood. The nitrogen content was the highest in W2 wood and lowest in W3 wood. Total carbon content in W3 was the highest (50.5%) among the studied three wood species which was in line with the results from proximate analysis. Oxygen contents calculated by the difference i.e., O%=100-(C+N+H)%, were 40.2, 34.4 and 34% respectively in W1, W2 and W3.

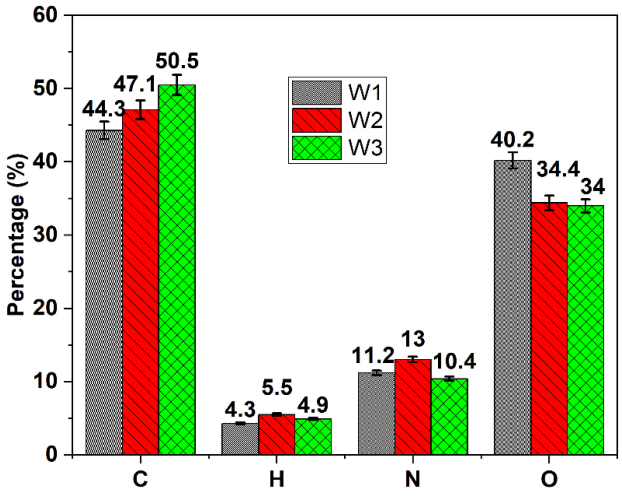

Figure 2.3 Ultimate values of biomass.

2.3.3 Thermal stability test

The variation in the thermal stability of different biomass species with increase in temperature is shown in Figure 2.4. Results showed that moisture removal region among the three species is essentially the same i.e., 40-120 ℃. Additionally, moisture removal rate was highest at approximately 60 ℃. Cellulose and lignin degradation temperature range was different for the three species. Temperature range for cellulose degradation are 210-400, 190-400 and 200-380 ℃ in W1, W2 and W3 respectively. Figure 2.4a and b corresponding to W1 and W2 showed a shoulder at 300 ℃ marking the end of hemicellulose degradation. Figure 2.4c corresponding to W3 have no such feature. Temperature range for lignin degradation are wider (200-1100 ℃) in W1 and W3, whereas it is narrow (200-800 ℃) in case of W3. It implies that lignin degradation will finish early in W3 than W1 and W2 wood species. The thermal stability information of wood species will help in designing carbonization or charcoal making experiments.

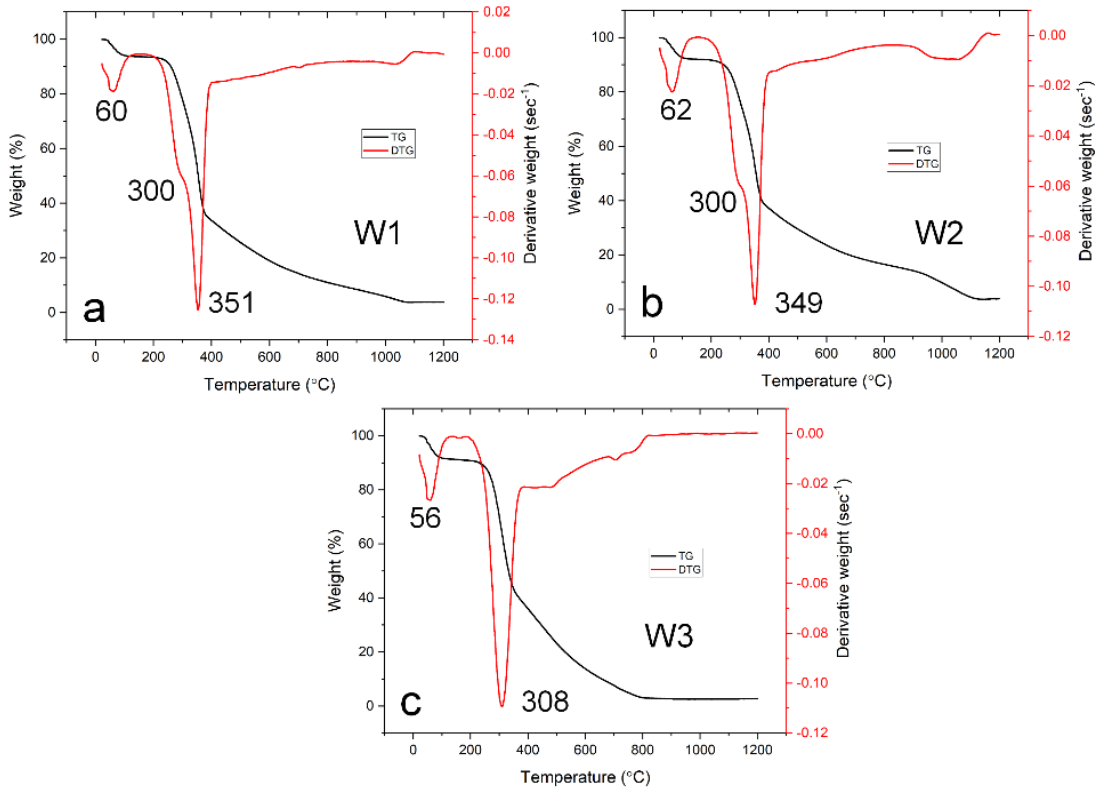

Figure 2.4 Thermal stability plots for a) W1, b) W2 and c) W3.

2.3.4 Specific gravity and Porosity

Measured values of the apparent and true specific gravity, and porosity for different woods are shown in Table 2.2. Tolerances represent the standard deviation. In general, all the three woods fall under the hardwood category. The true and the apparent specific gravity for W1 are the highest followed by W2 and W3. Apparent specific gravity accounts for bulk samples with closed pores whereas true sp. gravity accounts for solid particles without any pores or cavities. Therefore, the difference between the apparent and true sp. gravity values in the Table 2.2 indicates the high extent of porosity in the wood pieces. The values of porosity for these woods were fairly close, in the range of 59-62%.

Table 2.2 Physical properties of different woods.

S. No.	Wood species	Apparent sp. Gravity	True sp. Gravity	Porosity (%)
1	W1	0.67±0.04	1.62±0.08	58.64±4.26
2	W2	0.58±0.03	1.53±0.04	62.09±4.91
3	W3	0.58±0.03	1.51±0.06	61.58±4.43

2.3.5 Compressive strength

The results of compressive test of the woods are given in Table 2.3. In each loading direction, W1 possessed the highest compressive strength followed by W2 which was followed by W3. The compressive strength in T1 loading direction was the highest for W1 (58.52 MPa) followed by W2 (50.93 MPa) and W3 (31.41 MPa). The compressive strength in T2 and T3 loading directions was the highest (40.06 MPa) for W1 followed by W2 (32.71 MPa) and W3 (29.02 MPa). Specific gravity and the compressive strength in all the three orthogonal directions followed the above trend. Specific gravity of the wood is directly proportional to the load carrying capacity or the compressive strength of a wood (Table 2.2 and Table 2.3) [124]. The

age of the tree and location of the wood sample on the tree trunks might affect the reproducibility of the data on which the authors do not have information.

Table 2.3 Results of the compression test in longitudinal (T1) and transverse (T2 and T3) directions on different wood species.

Serial	Wood species	Loading plane	Compressive strength (MPa)	Energy consumed in breaking (J)
1	W1	T1	58.52±3.13	7.6±0.2
		T2	40.06±2.04	5.2±0.2
		T3	45.88±2.19	5.6±0.3
2	W2	T1	50.93±3.42	6.4±0.2
		T2	32.71±2.34	4.4±0.3
		T3	35.59±2.89	4.6±0.4
3	W3	T1	31.41±3.09	4.0±0.2
		T2	29.02±1.46	4.2±0.3
		T3	26.76±2.73	3.3±0.3

The greater the surface area offered by a wood, higher is the extent of reaction during the carbonization. In the present study, pores were in micron size range and for carbonization to occur hot air inside the furnace should enter the pores which was facilitated by larger pore sizes. Pores play an important role in influencing the extent and rate of carbonization.

2.3.6 SEM analysis

The fiber morphology of different (i.e., W1, W2 and W3) woods is shown in Figure 2.5 and Figure 2.6 at 2000× and 5000× magnification respectively. The void spaces (i.e., the pores) inside the porous fibers that run longitudinally, are clearly visible. In Figure 2.6, the densely-packed fibrous cells of cellulose in woods are seen. The fibers make the wood hard and strong. Figure 2.6 shows the pore structures and fiber arrangement more clearly at higher

magnification. W3 is having a uniform and oval shaped pore, W1 has non-uniform oval and rounded pores while W2 has non-uniform polygonal pores. The average pore sizes in W1, W2 and W3, measured using ImageJ software, were 15 μm, 13 μm and 26 μm with standard deviation of 1.7, 1.4, 1.9 μm respectively. Each pore has its own wall, that is to say that each fiber (visible clearly in T2 and T3 directions) is a hollow cylinder with a shell thickness the same as the thickness of the pore wall of ≈ 2 μm.

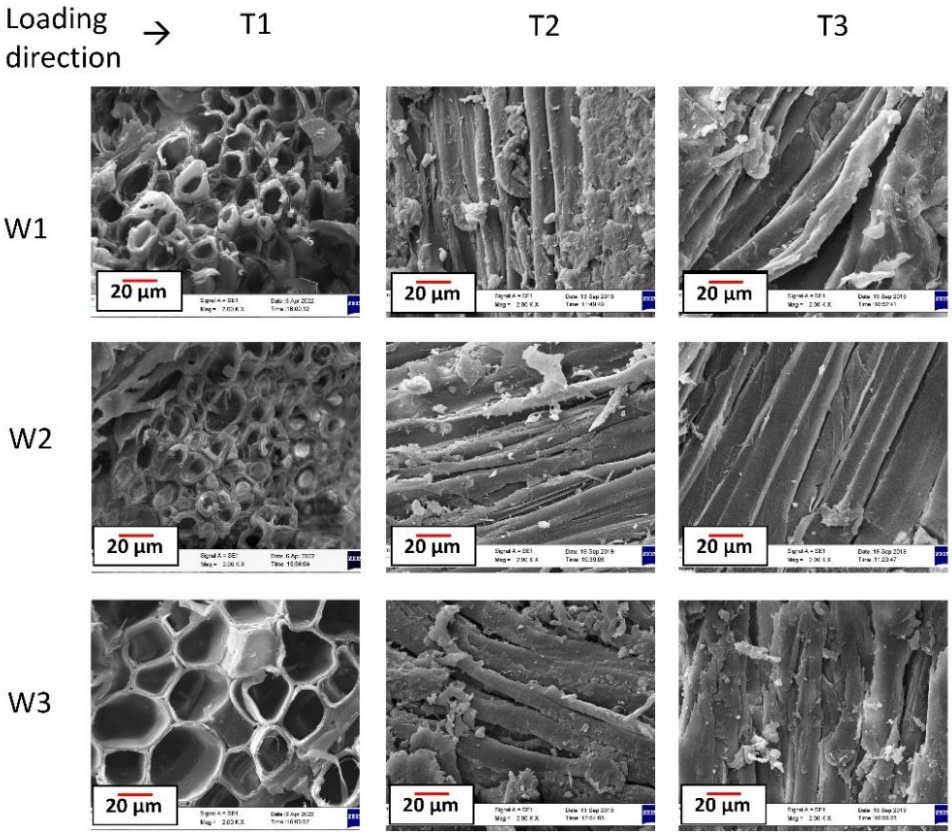

Figure 2.5 SEM images of different wood species in different directions.

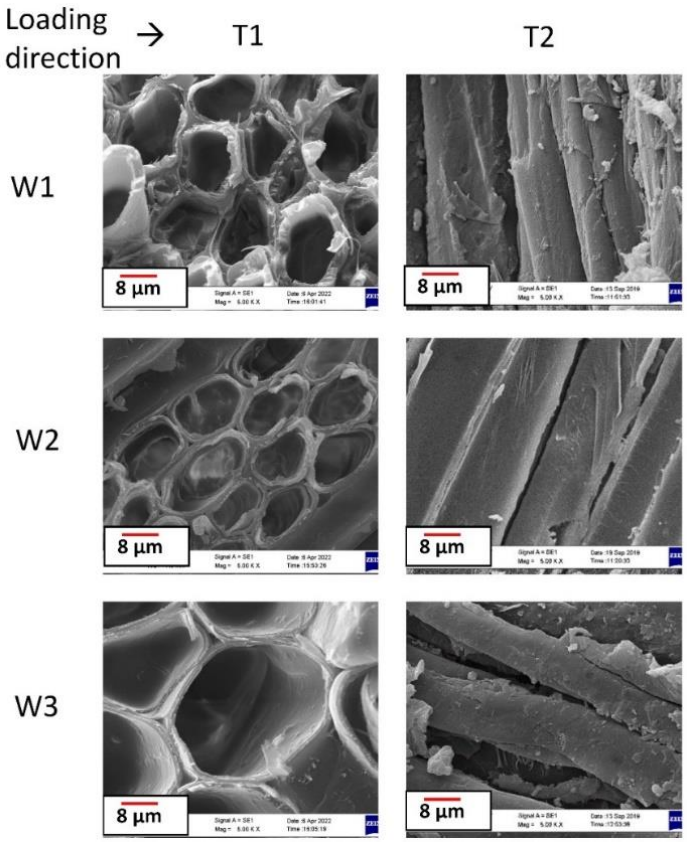

Figure 2.6 SEM images of different wood species in different directions.

2.4 Conclusions

Three hardwood species *Acacia nilotica* (W1), *Albizia lebbeck* (W2), *Leucaena leucocephala* (W3) were characterized for application in ironmaking. The results of proximate analysis, ultimate (CHNS) analysis, thermal stability test, apparent specific gravity, true specific gravity, porosity, compressive strength, nature and morphology of wood fibers (SEM microscopy) led to the following conclusions:

1. The fixed carbon (proximate analysis) and total carbon (CHNS test) values were the highest in W3 and almost equal in W1 and W2. Among these species cellulose and lignin degradation completed till a temperature of 400 and 1100 ℃ respectively. Lignin degradation completes earlier (200-800 ℃) in W3 than W1 and W2 (200-1100 ℃) wood species. Thermal stability test on biomasses also helped determine charcoal making (i.e., carbonization) temperatures.

2. The specific gravity of W1 was found to be higher than W2 and W3 wood. The fibers in W1 were interlocked while the other two wood varieties showed straight fibers.
3. The compressive strength of W1 wood in all the loading directions was the highest followed by W2 and W3. Pore size in W3 (≈ 26 µm) wood was large compared to W1 (≈ 15 µm) and W2 (≈ 13 µm), as measured by the SEM image analysis. The strength and the pore size appear highly correlated: smaller the pores stronger was the wood.