Preface

Steel is the most important engineering and construction material used globally. There are three industrial routes for steelmaking practiced around the globe. First and the most popular is the blast furnace-basic oxygen furnace (BF-BOF) route constituting 70% of total global steel production. Other two routes are steel scrap melting in electric arc furnace or induction furnace (Scrap-EAF/IF) route and direct reduced iron melting in electric arc furnace (DRI-EAF). Among these processes, BF-BOF and DRI-EAF routes directly use fossil coal. Blast furnace uses coke made by carbonization of metallurgical grade coal. Fossil coal is used in powder form for DRI making. Coal is formed in over 100 million years and final product of burning of fossil coal or coke is carbon di-oxide (CO_2). Level of CO_2 has increased to dangerously high level of 419 ppm by Feb 2023, which was 295 in pre-industrial time (1850). Iron and steel industry alone produces 2.6 Gt of CO_2 which is 7% of total global industrial emissions. CO_2 as a green-house gas is more deleterious in the sense that it constitutes of 70% of the total green-house gases and it absorbs 15 μm photon in infrared region which otherwise could easily pass-through earth's atmosphere. Increase in concentration of CO_2 is leads to increase in the extent of green-house effect causing global warming. Harmful effects of global warming are already prevailing. If not checked in time, global warming and its aftereffects will be catastrophic to life on the planet. To avoid these problems timely steps should be taken to reduce and substitute the use of fossil coal.

Chapter 1 deals with **literature review on the use of biomass in ironmaking, objective and plan of the work**. In the context of iron and steelmaking, the literature provides two alternatives to fossil coal i.e., green hydrogen and renewable biomass. Literature projects hydrogen as the best alternative from ironmaking process point of view. However, availability of green hydrogen, especially at the industrial scale is currently a bottleneck. The wood charcoal is another alternative mentioned in the literature. Wood charcoals have poor compressive strength compared to coke and hence it cannot replace coke in blast furnace.

Biomass can partially substitute coal in conventional (BF-BOF) route; it can fully substitute the coal in the alternative DRI-EAF route. In this thesis, application of charcoal in alternative DRI-EAF route is explored. Selection of wood species suitable for Indian soil & climate and their characterization followed by charcoal preparation and use of the charcoal for DRI preparation and its exploration in steelmaking was planned and demonstrated successfully.

Chapter 2 deals with **selection and characterization of suitable wood species**. Fast growing, high carbon yielding wood species suitable for short rotation forestry were shortlisted. Among them, two biomass species, hitherto unemployed towards this goal, i.e., *Albizia lebbeck* (W2) and *Leucaena leucocephala* (W3) were selected for wood charcoal preparation and *Acacia nilotica* (W1), was also studied to make comparison. Selected wood species were characterised using proximate analysis, ultimate analysis, thermo-gravimetric analysis (TGA), specific gravity & porosity measurements, compressive strength and scanning electron microscopy imaging. The fixed carbon (proximate analysis) and total carbon (CHNS test) values were the highest in *Leucaena* (W3) and almost equal in *Acacia* (W1) and *Albizia* (W2). TGA plots showed that moisture removal was completed over the same temperature range of 40-120 °C across the selected species. Cellulose degradation region occurred over a temperature range of 210-400 °C (W1), 190-400 °C (W2) and 200-380 °C (W3). A shoulder at 300 °C in the TGA plots of W1 and W2 marked the end of hemicellulose degradation which was absent in W3 wood. The specific gravity of W1 was found higher than W2 and W3 wood. 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.

Chapter 3 deals with **biomass carbonization and characterization of produced charcoals**. Selected species were carbonized for 1 hour at 600, 800 and 1100 °C to prepare wood charcoal which were characterized using proximate analysis, ultimate analysis, charcoal yield, volume shrinkage, compressive strength (using universal testing machine), scanning electron microscopy, Fourier transform infrared spectroscopy (FT-IR) and Raman spectroscopy techniques keeping in view of their targeted application in ironmaking. Charcoals were further characterized by CO_2 reactivity tests to evaluate their reactivity towards carbon di-oxide. Influence of parameters such as CO_2 gas flow rate, reactivity test temperature, carbonization temperature of charcoals and charcoal species were studied. Produced charcoals had comparable (superior in some cases) chemical compositions and energy content to metallurgical coke. 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. 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. FT-IR spectra demonstrated the degradation of lignin to form turbostratic or non-crystalline carbon. Raman spectra analysis suggested *Leucaena* char has the highest amount of disordered/turbostratic carbon and *Acacia* has the lowest among the charcoals studied. CO_2 Reactivity increased monotonically with increase in the reaction temperature from 850 to 1000 °C across wood species. Among 600, 800 and 1100 °C of carbonization temperatures, charcoals formed at 800 °C were found to be most reactive. Among different charcoal species, W3 was most reactive at a reactivity temperature of 900 °C, W2 at 950 °C. At reactivity temperature of 1000 °C, reactivity values are comparable among charcoal species with W3 exhibiting a marginally high value. Higher porosity, disordered carbon content and CO_2 reactivity make charcoal a better reducing agent. Therefore, W2 and W3 are potentially better reductants than W1 for ironmaking via the direct reduction route.

Chapter 4 deals with **preparation of DRI using the charcoals**. DRI were prepared at reduction temperatures of 800-1000 °C from iron ore and charcoal composite pellets to use in emerging rotary hearth furnace (RHF). Factors influencing the iron ore reduction such as C/O ratio, carbonization temperature (to produce charcoal), reduction temperature and the reduction time were studied. Reduction kinetics was studied by fitting various equations corresponding to reaction controlling steps such as gasification, diffusion or chemical reaction control to the experimental data. For complete reduction and maximum utilization of charcoals in the composite pellets, a value of 1.5 was found as the optimum C/O ratio. Each of the wood species, yielded the highest %R when carbonized at a temperature of 800 °C, due potentially to a higher reactivity of the carbon towards CO_2. For composite pellets with each charcoal species, maximum %R was obtained at a reduction temperature of 1000 °C at a reduction duration of 30 min. Composite pellets with W3 (83%) charcoal had the highest %R and W2 (70%) exhibited the lowest among the selected charcoals. The results were also corroborated by the XRD and SEM analysis. The activation energy for composite pellets was found lowest with W3 (169.9 kJ/mol) charcoal and highest with W2 (213.2 kJ/mol). Overall reduction reaction of the composite pellets was controlled by diffusion of the reactant gas followed by gasification of the charcoal. Results from reduction tests suggested that among the selected biomasses, *Acacia* (W1) and *Leucaena* (W3) are better reductants than *Albizia* (W2) charcoal.

Chapter 5 deals with the **exploration of the DRI use in steelmaking** by melting. The DRI, made under the optimized conditions determined in the Chapter 4, was melted in a horizontal tube furnace as well as in an electric arc furnace. Compositional and microstructural characterization of the resulting green steel was carried out and compared to a mild steel. The DRI melted in the electrical resistance heating tube furnace had slag and metal phases intermixed due to inadequate temperature and the absence of stirring. The steel made by melting the DRI in the mild steel pool had compositions and microstructure of low carbon steel with lower phosphorous and sulphur than the mild steel. The steel made this way can be termed as a green steel.

Chapter 6 deals with **conclusions** and Chapter 7 with **future scope** of the work.