Substitution of Coal by Renewable Reductants for Green Steelmaking

Thesis submitted in partial fulfilment

for the award of degree

Doctor of Philosophy

by

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February 2023

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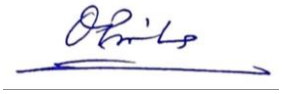

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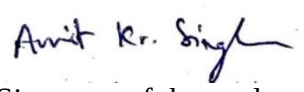

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Acknowledgements

I am very grateful and indebted to my supervisors, Prof. OP Sinha and Dr Randhir Singh, for their consistent supervision, guidance, encouragement and timely support during the entire period of my PhD at IIT BHU, Varanasi. Beside my supervisors, I would like to thank my RPEC members Dr JK Singh and Prof. Arif Jamal for their critical and insightful comments during semester evaluations. I would like to express my sincere gratitude to Prof. RC Gupta (former professor and head of the department, IIT BHU Varanasi) for his technical inputs and support in my PhD work.

I am grateful Prof. Sunil Mohan, Head of the Department and former Heads Prof. NK Mukhopadhyay and Prof. RK Mandal for allowing me to use facilities at their disposal, encouragement and support. I am also thankful to all the faculty members in the department for their inputs, encouragement and support. I am thankful to our scientific officer Dr LS Rao for always helping me out. I am also thankful to all the Lab staffs and office staffs of the department.

I would like to thank my friends, seniors, juniors and batchmates (especially, Dr Arup Kumar Mandal, Dr Rajkumar Dishwar, Dr Sharvan Kumar, Biswajit Mishra, Gautam Mishra, Raman Hissariya) for making this journey easy and memorable. Last but not the least, I would like to thank my family for cherishing and motivating me. Thank you all!

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.

Contents

List of Figures ix

List of Tables xi

Preface xii

Chapter 1 Introduction and literature review 1

1.1 Raw materials for steelmaking 2

1.2 Historical developments in steelmaking 3

1.3 Fossil fuel consumption and CO_2 emission by steel industry 5

1.3.1 Global initiatives at controlling the environmental damage 6

1.4 Use of hydrogen for green steelmaking 7

1.5 Use of biomass for green steelmaking 8

1.5.1 Blast furnace – Basic oxygen furnace (BF-BOF) route 10

1.5.2 Alternative routes 12

1.6 Objective of the present work 19

Chapter 2 Selection and characterization of biomass species for ironmaking 21

2.1 Introduction 21

2.2 Experimental 23

2.2.1 Procurement of raw materials 23

2.2.2 Characterization of biomasses 23

2.3 Results and discussion 27

2.3.1 Proximate analysis 27

2.3.2 Ultimate analysis 28

2.3.3 Thermal stability test 29

2.3.4 Specific gravity and Porosity 30

2.3.5 Compressive strength 30

2.3.6 SEM analysis 31

2.4 Conclusions 33

Chapter 3 Characterization of charcoals produced from *Acacia*, *Albizia* and *Leucaena* for application in ironmaking 35

3.1 Introduction 35
3.2 Experimental 38
3.2.1 Preparation of Charcoals 38
3.2.2 Characterization of charcoals 39
3.3 Results and Discussion 42
3.3.1 Proximate analysis 42
3.3.2 Ultimate analysis 43
3.3.3 Van Krevelen diagram 44
3.3.4 Charcoal yield 45
3.3.5 Volume shrinkage 46
3.3.6 Compressive strength 48
3.3.7 SEM analysis 49
3.3.8 Fourier transform infrared spectroscopy 51
3.3.9 Raman spectroscopy 53
3.3.10 Charcoal reactivity 55
3.4 Conclusions 57
Chapter 4 Reduction behavior and kinetics of iron ore-charcoal composite pellets for sustainable ironmaking 59
4.1 Introduction 59
4.2 Experimental 62
4.2.1 Raw materials 62
4.2.2 Methods 63
4.2.3 Characterization of DRI 65
4.3 Result and Discussion 67
4.3.1 Effect of C/O ratio 67
4.3.2 Effect of charcoal type and carbonization temperature 70
4.3.3 Effect of reduction temperature and time 71
4.3.4 Reduction Kinetics 75
4.4 Conclusions 79
Chapter 5 Exploration of the use of the DRI in steelmaking 81
5.1 Introduction 81
5.2 Experimental 82
5.2.1 Preparation of DRI in bulk 82

5.2.2 Methods 82
5.3 Results and Discussion 85
5.3.1 Electric resistance furnace melting 85
5.3.2 Electric arc furnace melting 87
5.4 Conclusion 89
Chapter 6 Overall conclusions 91
Chapter 7 Future scope 94
References 95
List of Publications I

List of Figures

Figure 1.1 Sector wise steel consumption in 2019 1
Figure 1.2 Crude steel production by top 5 countries 2
Figure 1.3 Raw materials, process flow and products in different steelmaking routes 3
Figure 1.4 Rising level of CO_2 in atmosphere 6
Figure 1.5 Formation and consumption time cycles for coal and biomass. 9
Figure 1.6 Prospects of using wood charcoal in steelmaking 12
Figure 1.7 Classification of direct reduction processes 13
Figure 2.1 Schematic wood cube showing three mutually perpendicular loading directions for compression test. 26
Figure 2.2 Proximate values of biomass. 28
Figure 2.3 Ultimate values of biomass. 28
Figure 2.4 Thermal stability plots for a) W1, b) W2 and c) W3. 29
Figure 2.5 SEM images of different wood species in different directions. 32
Figure 2.6 SEM images of different wood species in different directions. 33
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. 39
Figure 3.2: Schematic of the experimental setup employed for CO_2 reactivity tests 42
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. 43
Figure 3.4 a) Points showing variation in C, H and N values from wood to charcoal and b) Ternary diagram showing ultimate analysis values. 44
Figure 3.5 Modified van Krevelen diagram with charcoals and coke 45
Figure 3.6 Variation of charcoal yield with carbonization temperature for different biomasses in a) slow heating b) fast heating condition. 46
Figure 3.7 Variation of charcoal volume shrinkage with carbonization temperature for different biomasses in a) slow and b) fast heating condition. 48
Figure 3.8 Variation of compressive strength with carbonization temperature for different biomasses in a) slow and b) fast heating condition. 49
Figure 3.9 SEM images of a) W3 charcoals produced at different carbonization parameters, b) different charcoals produced at 1100 °C in fast heating. 50
Figure 3.10 FT-IR spectra for a) W1, b) W2. C) W3 Charcoals 52

Figure 3.11 Raman spectra of a) W1, b) W2. C) W3 charcoals. 54
Figure 4.1 Sieve analysis of a) iron ore powder, b) charcoal powder and c) proximate analysis of charcoals. 63
Figure 4.2 Schematic of the experimental setup employed for the composite pellet reduction. The components of the setup are: 1. Gas cylinder, 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. 65
Figure 4.3 Variation in %R and the overall rate of reaction with C/O ratio in the pellets prepared with W3 charcoal carbonized at 800 °C and reduced at 1000 °C. 69
Figure 4.4 Rate of reaction with time for different C/O ratio composite pellets with W3 charcoal carbonized at 800 °C. 69
Figure 4.5 Variation in %R with the type and carbonization temperature of the charcoal used in the composite pellet.. 70
Figure 4.6 Fractional weight with reduction temperature and time for different composite pellets at C/O ratio of 1.5 with W1, W2 and W3 charcoals carbonized at 800 °C. The percentage figures on the right are %R which corresponds directly to the fractional weight change. 72
Figure 4.7 SEM micrographs of the DRIs produced from the reduction iron ore-wood charcoals of W1, W2 and W3, composite pellets. Reduction temperature: 1000 °C, reduction duration: 30 min and C/O ratio: 1.5 were used. 74
Figure 4.8 X-ray diffraction plots for iron ore composite pellets with W1, W2 and W3 charcoals at a reduction temperature of 1000 °C and reduction duration of 30 min. 74
Figure 4.9 Fitting of the selected models to the experimental data for iron ore charcoal composite pellets with W1 (a, b and c), W2 (d, e and f) and W3 (g, h and i) charcoals at different reduction temperatures. 77
Figure 4.10 ln(k) vs $10^4/T$ plot for iron ore charcoal composite pellets. 78
Figure 5.1 Schematic of crucible and furnace used for reduction experiments. 84
Figure 5.2 Tapping of the melt in a graphite crucible..... 84
Figure 5.3 Microstructures showing constituents of the solidified melt (melted in a resistance furnace) under a) optical microscope and b) scanning electron microscope. 86
Figure 5.4 Elemental distribution in the slag and metal phase in air melt sample 86
Figure 5.5 Composition corresponding to EDS spots in the SEM image of air melt. 87
Figure 5.6 SEM micrograph showing a) ferrite and pearlite at 5000× magnification and b) ferrite and iron carbide lamellae at 20000× magnifications in EAF melt..... 89

List of Tables

Table 1.1 Application of biomass derived charcoals for mitigation of CO_2 emission in different ironmaking processes 10
Table 1.2 Prior studies performed on various hardwood biomasses in view of their potential use in direct reduction of iron ore. 16
Table 2.1 Geoclimatic requirements for cultivating selected hardwood species 23
Table 2.2 Physical properties of different woods. 30
Table 2.3 Results of the compression test in longitudinal (T1) and transverse (T2 and T3) directions on different wood species. 31
Table 3.1 Pore and intrapore sizes for charcoals shown in Figure 3.9b. 51
Table 3.2 Deconvoluted Raman spectra peak characteristics. 54
Table 3.3 Variation of reactivity with CO_2 gas flow rate at reactivity temp of 950°C with W3 charcoal carbonized at 600 °C 55
Table 3.4 Variation of charcoal reactivity with reactivity temperature, for charcoals prepared at 600 °C 56
Table 3.5 Variation of reactivity with charcoal species carbonized at 600 °C 56
Table 3.6 Variation of reactivity with carbonization temperature at reactivity temp of 950 °C 57
Table 4.1 Calculation of %R and %M for composite pellets at different reduction temperatures for different charcoals as shown in Figure 4.6. 72
Table 4.2 Activation energies for the reduction of iron ore with W1, W2 and W3 charcoal composite pellets. 79
Table 5.1 Composition of the mild steel and the EAF melt 88