

Chapter 4 Reduction behavior and kinetics of iron ore-charcoal composite pellets for sustainable ironmaking

Charcoals characterized in the chapter 3 were used in the present chapter to make composite pellets with iron ore. Effect of C/O ratio, carbonization temperature, reduction temperature, reduction time and the charcoal types on the reduction behaviour of iron ore charcoal composite pellets were studied. Reduction kinetics was studied using three popular models.

4.1 Introduction

Mining and processing of iron ore generate waste fines. Likewise, coal mining also results in fine generation which finds little use. Several researchers have mixed and agglomerated iron and coal fines to make self-reducing composite pellets [168-178]. These composite pellets were processed in solid state in a rotary hearth furnace to make directly reduced iron (DRI). These pellets have high reducibility as iron ore and coal fines are intimately mixed. Effect of the processing parameters like C/O ratio (defined as ratio of the moles of carbon in the charcoal to the moles of oxygen bound to iron in the ore present in the composite pellet), reduction temperature, reduction time, iron ore and coal particle size, pellets size and inert atmosphere on the reduction behaviour have been extensively studied. The rate of the reduction defined as change in %R of the pellet per unit time, is very fast at the beginning and decreases continuously with time [168-170]. It increases with an increase in reduction temperature [171-173]. At a typical temperature of 1000 °C, the rate of reduction increases monotonically as C/O or C/Fe₂O₃ ratio increases [174-178].

The reduction kinetics of composite pellets have also been studied by various researchers [168-170, 173, 174] using different approaches to develop models for the reduction process. The overall reduction process is demonstrated to proceed in two parallel stages:

i) reduction of Fe_2O_3 successively to Fe by CO and ii) generation of CO by the solution loss or carbon gasification reaction ($\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$) [168, 169]. CO_2 produced from reduction reaction combines with carbon from the coal to form CO, which is known as the solution loss reaction. The solution loss reaction is the dominant mode of producing CO and is hence believed to be the rate-limiting step for the overall process [168, 174, 179, 180].

In addition to the non-renewable coal, researchers have also explored CO_2 neutral charcoal as a reductant in iron ore composite pellets. Biomass derived charcoals have higher reactivity towards CO_2 than fossil coal enabling over 100 °C lower reduction start temperature (about 800 °C) [72, 73]. Higher reactivity is due to amorphous nature of wood charcoal [74]. The maximum reaction rate in case of charcoal is approximately 1.5 times the rate obtained with coal and concomitant with much higher reduction extent [72, 73]. Iron oxide (mill scale) reduced with charcoal achieved a total iron content of 98.56%, with the metallization ratio of 99.25% [75]. A reduction temperature of 1200 °C and reduction duration of 20 mins are sufficient for complete reduction of composite pellets [76]. Iron ore composite pellets reduced at 1000 °C with charcoal derived from hardwood attained a reduction of over 90% [77]. Increasing the amount of charcoal in composite pellets increases the rate and extent of reduction [73]. Increasing the heating rate promotes reduction rate efficiently up to 20 °C/min [78]. Reduction sequence is the same as in reduction of iron ore and coal composite pellet i.e., $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$ [78-81]. The activation energy for the charcoal reduction reported in literature is in the range of 59 to 160 kJ/mol [65, 87, 88].

Yuan et al. [88] used coke, coal, and charcoal as reductants in a comparative investigation on the reduction kinetics of iron ore composite pellets. Charcoal was produced at a carbonization temperature of 900 °C under a nitrogen atmosphere. The authors reported that in comparison to coke and coal, charcoal has a faster reduction rate at a lower reduction temperature. Effect of the reducing agent on the reduction rate weakened with an increase in reduction temperature.

Reduction rates among the three composite pellets became almost equal at reduction temperature of 1200 °C. The overall reduction reaction of the three pellets were reported to be gas diffusion controlled. The activation energies for reduction of composite pellets with coke, coal and charcoal were 96, 72 and 59 kJ/mol, respectively. The composite pellets containing charcoal required much lower activation energy for the reduction reaction. Konishi et al. [77] carbonized Japanese cypress at 550, 800 and 1000 °C. Composite iron ore (hematite) and charcoal pellets were prepared in the mass ratio of 1:4. The pellets were reduced at reduction temperatures of 800, 900 and 1000 °C in nitrogen atmosphere. The authors reported that at each reduction temperature, fractional reduction was the highest with charcoals carbonized at a carbonization temperature of 550 °C.

In a nitrogen environment, Hu et al. [181] investigated the influence of iron ore concentration and temperature on the reduction behaviour of iron ore and biochar composite pellets. Interestingly, the authors studied reduction reaction in terms of produced CO and CO₂ gas during reduction. The authors varied the carbon to iron ore mole ratio in composite pellets from 0.54 to 4.83 and reported a value of 3.22 as optimum based on %R. The authors also reported that upon increasing the temperature from 700 to 1000 °C, %R increased from 17 to 70%. Authors further reported that iron ore reduction was controlled by three-dimensional diffusion. Wang et al. [78] reduced Fe₂O₃ as composite pellets using four different biomasses i.e., rice lemma, maize cob, peanut hull and pine sawdust. The reduction reactivity varied as maize cob >peanut hull >pine sawdust >rice lemma. Yuan et al. [85] studied reduction of iron ore composite pellets with cheap biomass charcoals such as straw fibre, bamboo char, tree branch pruning and compared their performance with graphite and anthracite coal. Authors reported an optimum reduction temperature, time and C/O ratio as 1200 °C, 20 min and 0.7 respectively. Composite pellets with straw fibre showed higher reducibility during the entire reduction process. Authors also reported that volatiles in the charcoal enhance the reducibility of such pellets when compared to composite pellets of anthracite coal and graphite. Usui et al. [74]

reduced reagent grade hematite with three types of coal char and two type of wood charcoal from Japanese cedar and cypress. Authors reported that hematite composite pellets with wood charcoals had higher rate of reduction than any of the selected coal char pellets because of higher gasification rate of wood charcoals. Reduction reaction started at 560 °C in N₂ atmosphere for wood charcoal carbonized at 550 °C. The reactivity of the produced charcoal decreased with increasing carbonization temperature from 550 to 1000 °C which was in line with finding by Konishi et al. [77].

These studies establish that wood charcoal is more reactive than coal and coke during reduction of iron ore charcoal composite pellets. However, charcoals from the fast-growing and high carbon yielding hardwood biomasses such as *Acacia*, *Albizia* and *Leucaena* have not been exploited in the reduction of iron ore-charcoal composite pellets. Renewable biomass produced by the short rotation forestry method can be utilized to limit CO₂ emissions produced during the ironmaking process. The objective of the present work is to study the reduction potential and kinetics of high carbon yielding and fast-growing hardwood biomass charcoals in the iron ore-charcoal composite pellets. Selected biomass charcoals were produced from *Acacia nilotica* (W1), *Albizia lebbeck* (W2), *Leucaena leucocephala* (W3).

4.2 Experimental

4.2.1 Raw materials

Hematite iron ore fines (-15 mm) assaying Fe₂O₃-92.5 wt%, Al₂O₃-3.7 wt%, SiO₂-2.94 wt% and LOI-4.9 wt% were procured from one of the mines of Tata Steel Jamshedpur, India. Sieve analysis of the iron ore and charcoal as per ASTM C136-01 are presented in Figure 4.1a and b. Charcoals were prepared at the carbonization temperature of 600, 800 and 1100 °C with a heating rate of 50 °C/min in a mild steel retort with a top cover. More details about the chemical and physical properties of the charcoals are available in chapter 3, section 3.3. Proximate analysis of charcoals is presented in Figure 4.1c.

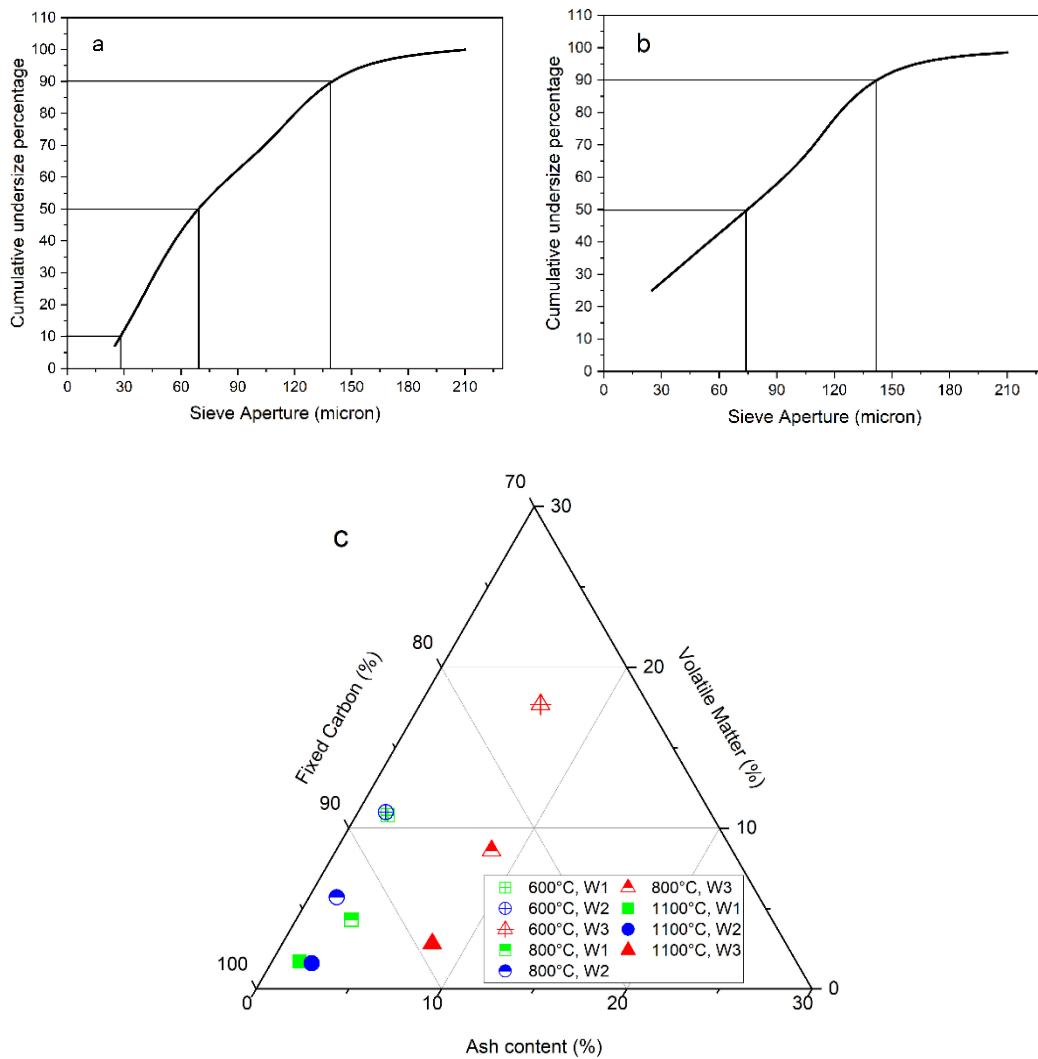


Figure 4.1 Sieve analysis of a) iron ore powder, b) charcoal powder and c) proximate analysis of charcoals.

4.2.2 Methods

Iron ore fines were first crushed in a roll crusher. Iron ore fines and charcoals were then ground separately and sieved to $-210 \mu\text{m}$ and stored in desiccators. The iron ore and charcoal fines were mixed thoroughly in definite proportions and blended with water. No other binders were used. The blend was pelletized to make $-19 +9 \text{ mm}$ diameter green composite pellets according to IS-11092:2001 [182] weighting ≈ 3 grams. Green composite pellets were air-dried for 24 hours before being dried in an oven at $100 \pm 5 \text{ }^\circ\text{C}$ for another 24 hours. A Thermo-Gravimetric (TG) type setup shown schematically in Figure 4.2 was used to study the reduction behaviour of composite pellets. After a set temperature in the vertical tube furnace was reached, a single pellet was loaded in the platinum basket and hanged at the bottom of the transparent quartz

tube, away from the heating zone. Nitrogen was purged for 5 mins at a rate of 1 L/min to flush out air inside the quartz tube. The rate of flow of nitrogen was reduced to 0.5 L/min after 5 mins. The basket with the pellet, 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 every minute during the reduction time of 30 min. After completing the reduction experiment, the platinum basket with DRI was lowered at the bottom end of the quartz tube and cooled in nitrogen gas to room temperature. The DRI was then stored in a desiccator for further analysis. The same procedure was precisely followed in every experiment.

To optimize the amount of charcoal in the composite pellets, the C/O ratio was varied from 1 to 2.5. C/O ratio was defined as the ratio of number of moles of carbon in the charcoal to number of moles of oxygen in the ore. For unit C/O ratio, 57.7 g of hematite ore (assaying 92.5% of Fe_2O_3 in iron ore) having 1 mole of oxygen in Fe_2O_3 requires 12.9 g of charcoal (say W2 charcoal produced at 800 °C has 93% carbon) having 1 mole of carbon. This relation was used to calculate the weight of charcoal needed for specific C/O ratio given the weight of iron ore. Reduction of composite pellets was performed using charcoals produced at 600, 800 and 1100 °C to optimize the carbonization temperature. The effect of the charcoal type along with the reduction temperature and time on the reduction behaviour was studied. Reduction temperature was varied from 850 to 1000 °C in 50 °C steps and the reduction duration were fixed for 30 min in each experiment. To ensure repeatability, each experiment was repeated thrice and the standard deviation in the data is shown as error bars. Reduction kinetics was studied employing models discussed in section 4.4. Activation energies were calculated for reduction of composite pellets with different types of charcoals.

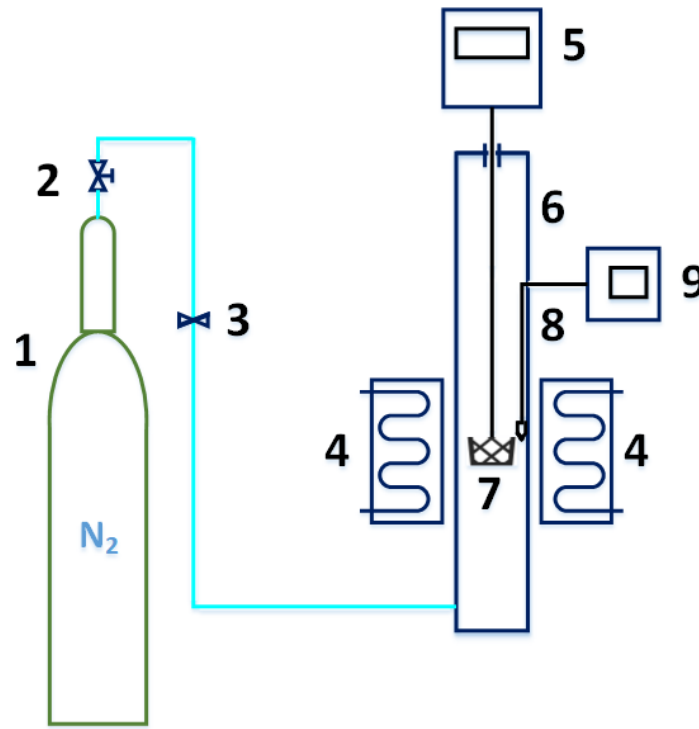


Figure 4.2 Schematic of the experimental setup employed for the composite pellet reduction. The components of the setup are: 1. Gas cylinder, 2. Gas regulator, 3. Gas flowmeter, 4. Cylindrical resistance furnace, 5. Weighing scale, 6. Quartz tube with ID: 44mm, 7. Platinum wire with Platinum basket, 8. Thermocouple, 9. PID controller.

4.2.3 Characterization of DRI

For a composite pellet system, Yang et al. [183] assumed that CO generated from carbon gasification is used for reduction of iron ore. They defined **%Reduction** (%R) as a ratio of the weight loss of pellet (the numerator in the Equation 4.1) to the theoretical weight loss of pellet (the denominator in the Equation 4.1), assuming complete reduction of hematite via the overall reaction as: $\text{Fe}_2\text{O}_3(\text{s}) + 3\text{C}(\text{s}) \leftrightarrow 2\text{Fe}(\text{s}) + 3\text{CO}(\text{g})$. The same formula (Equation 4.1) was used to calculate the %R of composite pellets in the present study. Hematite content in selected ore was 92.5 wt% and only the weight of the hematite was considered in the calculation of W_o .

$$\%R = \left[\frac{(W_o - W_f)}{W_o \times \frac{3 \times M_{CO}}{M_{Fe_2O_3} + 3 \times M_C}} \right] \times 100 \quad (4.1)$$

where,

W_o = Weight of the composite pellet before reduction,

W_f = Weight of the composite pellet after reduction,

M = Molar mass (g/mol) of the species mentioned in the subscript.

%Metallization (%M) was evaluated by titration based chemical method according to IS 15774. The procedure gives the total metallic iron, Fe(M), in the reduced pellet. Total iron content, Fe(T), in the composite was calculated from XRF of the iron ore. 1 g of the reduced sample was transferred in a 500-ml conical flask and 200 ml of ferric chloride solution was added. The flask was covered with a stopper and was agitated with polypropylene coated magnetic stirrer for 1 h. The solution was filtered through medium texture filter paper and the residue was washed with ferric chloride solution. The filtrate was transferred to a one-litre beaker containing 400 ml water, 25 ml sulphuric acid (98% v/v), 25 ml phosphoric acid (88% v/v), 3 to 4 drops of sodium diphenylamine sulphonate (as indicator) and titrated with potassium dichromate solution (0.1 N). 1 ml 0.1 N $K_2Cr_2O_7$ consumption during the titration is equivalent to 0.001862 g of metallic iron Fe(M) in the titrand. %M is calculated as per equation 4.2.

$$\text{Metallization(\%)} = \frac{\text{Fe(M)}}{\text{Fe(T)}} \quad (4.2)$$

The reduced DRIs were characterized using **X-ray diffraction** for different phases present. A PANalytical EMPYREAN HR-XRD (Co $K\alpha$ radiation, acceleration voltage = 40 kV, λ = 1.78901 nm and beam current = 40 mA, range = 10–100 deg, scan rate = 4 deg/min) was used to analyse the distinct phases in the DRI using the X'pert High Score software. A **scanning electron microscope** (SEM; model ZEISS EVO-18, INCA Energy 300 software from Oxford

Instruments, beam current ≈ 5 mA and acceleration voltage of 20 kV) was used to study the morphology of the DRI produced.

4.3 Result and Discussion

Important factors influencing the iron ore reduction are the C/O ratio, carbonization temperature to produce charcoal, reduction temperature and the reduction time. Effect of these factors are respectively presented in the below sub-sections. The reduction kinetics is studied in section 4.3.4.

4.3.1 Effect of C/O ratio

The overall rate of reaction (weight loss/time) and %R at different C/O ratios are plotted in Figure 4.3. It shows that %R first increased with the C/O ratio of up to 1.5, it then decreases at 2 and increased again at a C/O ratio of 2.5. Various researchers [168, 171, 174, 181, 184-186] varied molar ratio of charcoal to iron ore and achieved an optimum value for achieving the maximum %R. Some researchers [168, 174, 184, 186] reported that the %R keeps on increasing monotonically with an increase in the amount of charcoal. At the same time, others [171, 181, 185] found that the %R increases, reaches a maximum and then decreases with increasing the C/O ratio.

In addition to the %R, the overall rate of reaction was chosen as the parameter for selecting the optimum C/O ratio. Figure 4.3 shows the variation of the overall rate of reaction (weight loss/time) over the initial 12 mins of the isothermal reduction with increasing C/O ratio. The overall rate of reaction increases attains a maximum at a C/O ratio of 1.5 and decreases with further increase in C/O ratio. The maximum %R and the overall rate of reaction values established a C/O ratio of 1.5 as the optimum. Thus, the C/O ratio was fixed at 1.5 in the following experiments.

Initial sweeping and continuous supply of nitrogen gas during the reduction ensured an absence of gaseous oxygen inside the quartz tube. In a composite pellet, oxygen from iron ore is the only available oxygen to react with the charcoal. As the amount of charcoal increases, carbon available to reduce the iron ore increases and hence the %R increased with an increase in the C/O ratio. There seems to be a critical point where carbon supplied from the charcoal is optimum for the maximum reduction of the iron ore. The use of charcoal in excess of the critical or optimum value reduces the amount of iron ore (effectively of oxygen) per unit volume of the pellet. Gasification and iron ore reduction reactions, generating CO and CO₂ respectively, are inter-dependent in the overall reduction of composite pellets. A relative decrease in the amount of iron ore in the composite pellet decreases the CO₂ generation and in turn suppresses the CO generation irrespective of the availability of excess carbon (charcoal). Lower availability of the CO for the reduction reaction in turn lowers the %R, although the pellet may have excess of solid reductant [171, 174, 181]. Furthermore, Fe₂O₃ to FeO conversion requires a CO/CO₂ ratio of 0.25 whereas FeO to Fe conversion requires 2.5 [168]. Increase in the %R, at the C/O ratio of 2.5 might be due to greater extent of FeO to Fe conversion owing to CO/CO₂ ratio greater than 2.5, possible with increased charcoal content.

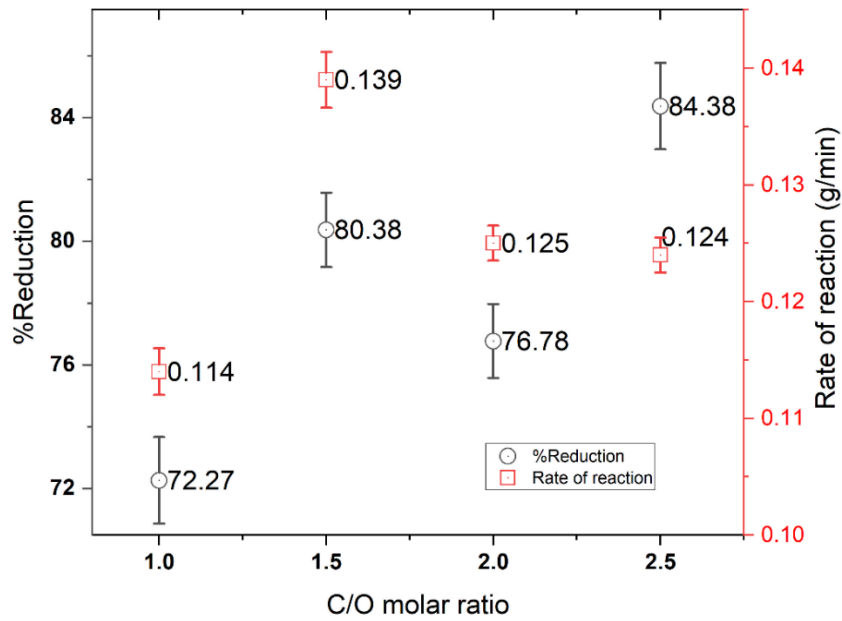


Figure 4.3 Variation in %R and the overall rate of reaction with C/O ratio in the pellets prepared with W3 charcoal carbonized at 800 °C and reduced at 1000 °C.

Figure 4.4 shows the variation in instantaneous rate of the reaction with time for different C/O ratios. It shows that the maximum instantaneous rate of reaction was attained with a C/O ratio of 1.5 the C/O ratio which was found optimum for the maximum %R.

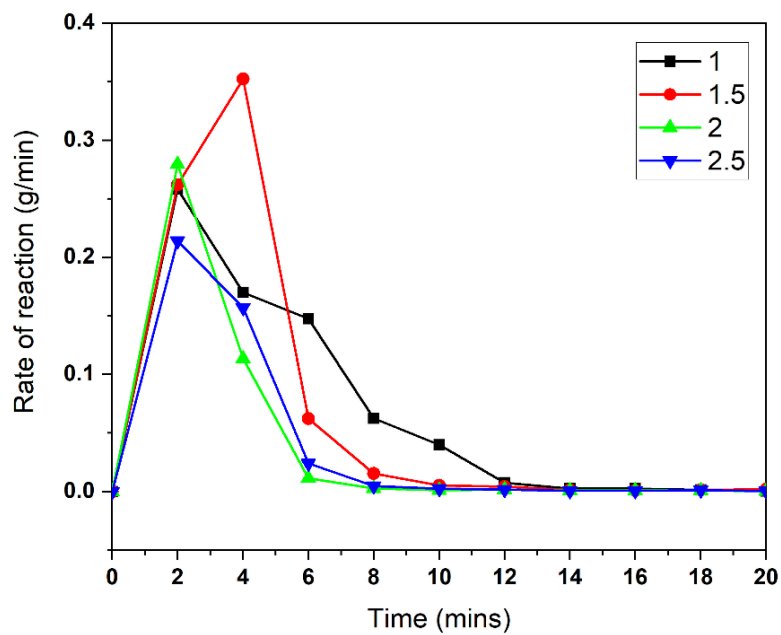


Figure 4.4 Rate of reaction with time for different C/O ratio composite pellets with W3 charcoal carbonized at 800 °C.

4.3.2 Effect of charcoal type and carbonization temperature

Reduction of iron ore was performed using charcoals prepared at carbonization temperatures of 600, 800 and 1100 °C from different wood species (W1, W2 and W3). %R for composite pellets with varying carbonization temperatures and charcoal types are plotted in Figure 4.5. Reduction temperature of 1000 °C and C/O ratio of 1.5 was selected for the reduction. It is evident from Figure 4.5 that type of charcoal and carbonization temperature has a significant impact on the %R of iron ore charcoal composite pellets. Composite pellets with W1, W2 and W3 charcoals were reduced to a %R of 55-81%, 50-71% and 63-83%, respectively. It is noticeable that composite pellets yielded the maximum %R, of 81.5, 70.9% and 82.5 for W1, W2 and W3, respectively, each carbonized at the same temperature of 800 °C. This means that W1 and W3 are more reactive than W2 charcoal. An initial increase followed by a decrease in %R value with an increase in carbonization temperature can be attributed to the reactivity of the charcoals. With thermal deactivation of the charcoal, the specific surface area increases somewhat with increasing temperature up to 805 °C, then falls due to structural ordering and micropore coalescence [97, 187, 188].

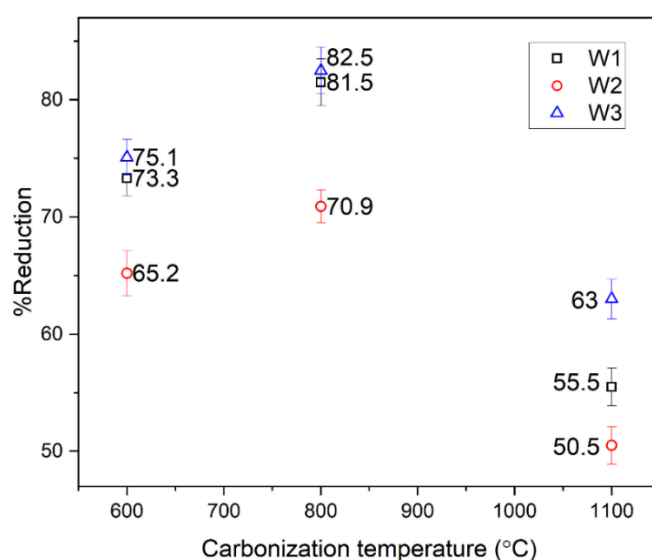


Figure 4.5 Variation in %R with the type and carbonization temperature of the charcoal used in the composite pellet. The reduction was carried out at 1000 °C with C/O ratio of 1.5 for 30 min.

4.3.3 Effect of reduction temperature and time

Fractional weight (instantaneous pellet wt / initial wt) at reduction temperatures of 850, 900, 950 and 1000 °C for W1, W2 and W3 charcoals are plotted in Figure 4.6. %R values are also reported alongside the fractional reduction plots. It is clear from Figure 4.6 that fractional weight decreased as reduction temperature and time increased, leading to an increase in %R. The same trend was noted by other researchers [171, 173, 189]. At low temperatures, the generation of CO and the reduction reactions are slow, lowering the overall rate and extent of reaction. With a rise in temperature, the gasification rate increases along with the rate of reduction because of an increase in the diffusion and chemical reaction rates [172]. This rise in gasification and reduction rates complement each other improving the overall reduction rate and extent at higher temperatures [169]. At all reduction temperatures, composite pellets with W3 charcoal had the highest %R and it was the lowest with W2. The rate of change in the fractional weight of the composite pellet with W1 charcoal increased very fast when the reduction temperature was raised from 950 to 1000 °C so much so that the %R with W1 charcoal moved very close to that of W3 charcoal. Enhanced rate of carbon gasification reaction in W1 charcoal above 950 °C could have increased the rate of reduction of iron ore, accelerating the loss in the fractional weight of the composite charcoal with W1. The maximum %R obtained was at the maximum isothermal reduction temperature of 1000 °C in composites with W1 (82%), W2 (70%) and W3 (83%) charcoals. The maximum %R obtained in the case of charcoal based composite pellets reduced at 1000 °C are higher than that obtained for coal based composite pellets reduced at 1250 °C for 20 minutes, which is up to 75% [185]. Data for the calculations of %R for composite pellets at different reduction temperatures for W1, W2 and W3 charcoals are compiled in Table 4.1. Corresponding %metallization (%M) evaluated from titration based chemical method are also compiled in the same table. It can be noticed that %M follows the same trend as %R.

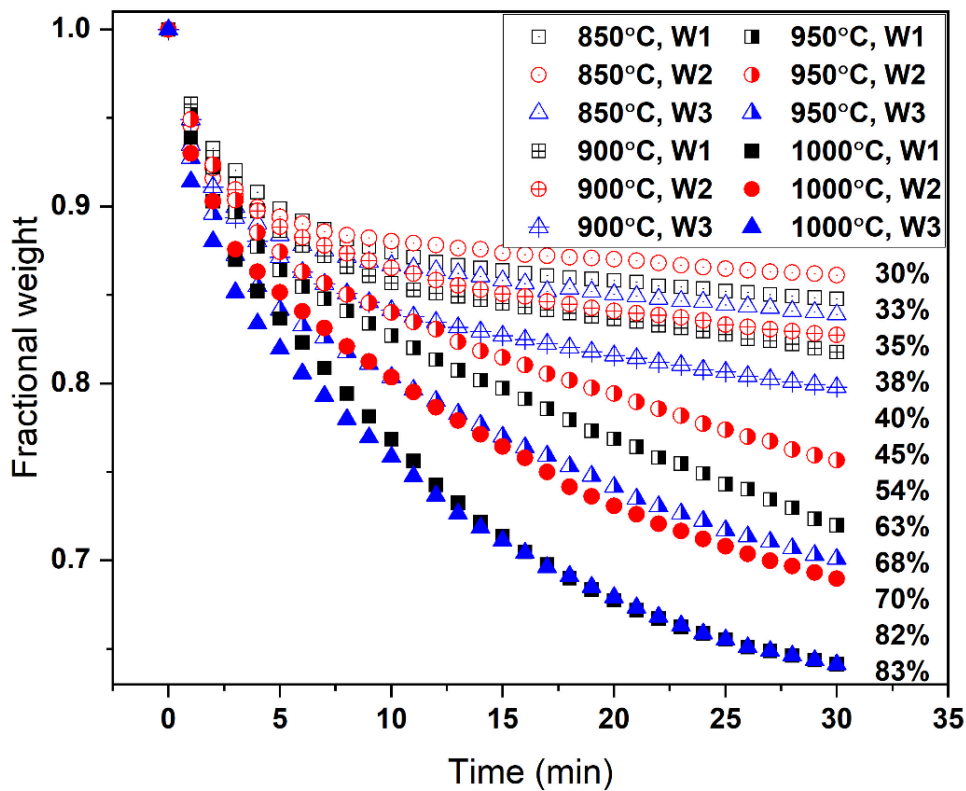


Figure 4.6 Fractional weight with reduction temperature and time for different composite pellets at C/O ratio of 1.5 with W1, W2 and W3 charcoals carbonized at 800 °C. The percentage figures on the right are %R which corresponds directly to the fractional weight change.

Table 4.1 Calculation of %R and %M for composite pellets at different reduction temperatures for different charcoals as shown in Figure 4.6.

Temperature (°C)	Charcoal type	Weight of pellet before reduction (g)	Weight of pellet after reduction (g)	Change in weight during reduction (g)	%R	%M
850	W1	3.515	3.018	0.497	33.02	4.9
850	W2	3.515	3.066	0.449	29.83	0
850	W3	3.407	2.895	0.512	35.05	7.81
900	W1	3.278	2.715	0.563	40.1	15.02
900	W2	3.278	2.747	0.531	37.82	11.76
900	W3	3.298	2.665	0.633	44.8	21.74
950	W1	3.18	2.318	0.862	63.23	48.09

950	W2	3.101	2.376	0.725	54.53	35.65
950	W3	3.13	2.222	0.908	67.71	54.49
1000	W1	3.071	1.995	1.076	81.76	74.57
1000	W2	3.101	2.166	0.935	70.34	58.25
1000	W3	3.15	2.03	1.12	82.97	76.3

SEM micrographs of DRIs produced at 1000 °C with W1, W2 and W3 charcoals are presented in Figure 4.7. The micrographs illustrated the fibrous growth morphology of iron whiskers. Small charcoal pieces along with iron whiskers were present. Thus, not all the charcoal was utilized even at an optimized C/O ratio. Furthermore, it indicated that the optimum value for C/O actually lied somewhere between 1 and 1.5. Relatively lesser growth of iron whiskers in the DRI with W2 charcoal, apparent from higher porosity, indicated a lower %R than with the W1 and W3 [190]. This is likely due to higher reactivity of W1 and W3 charcoals than the reactivity of W2 towards CO₂ at 1000 °C. More reactive the charcoal, higher is the extent of CO generation which is the main reductant to reduce the iron ore pellet.

XRD plots of the DRIs produced at the reduction temperature of 1000 °C with W1, W2 and W3 charcoals are presented in Figure 4.8. Plots show presence of metallic iron, amorphous carbon and non-stoichiometric FeO in DRIs. Among the reduction steps involved in iron ore to iron, reduction of FeO to Fe is the most complicated. Presence of non-stoichiometric FeO in DRIs conforms incomplete reduction of iron ore. Intensities corresponding to iron phase in DRIs produced with W1 and W3 charcoal are higher than the intensities in W2, indicating a higher amount of metallic iron in the former. These observations are in line with the approximately 12% higher %R of iron ore with W1 and W3 charcoals than the %R of iron ore with W2 charcoal in Figure 4.6.

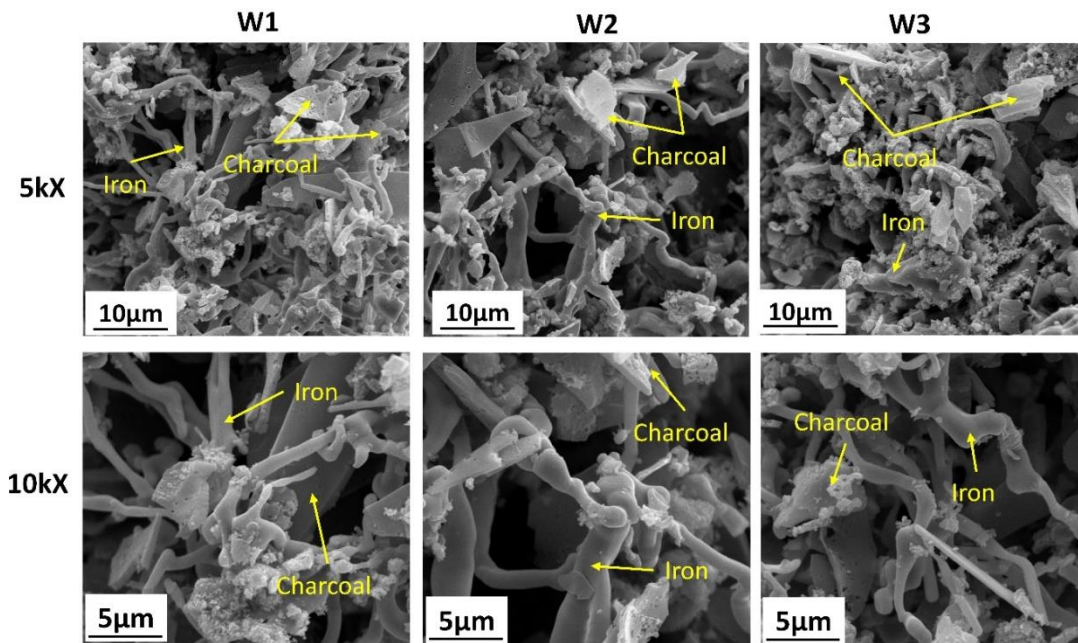


Figure 4.7 SEM micrographs of the DRIs produced from the reduction iron ore-wood charcoals of W1, W2 and W3, composite pellets. Reduction temperature: 1000 °C, reduction duration: 30 min and C/O ratio: 1.5 were used.

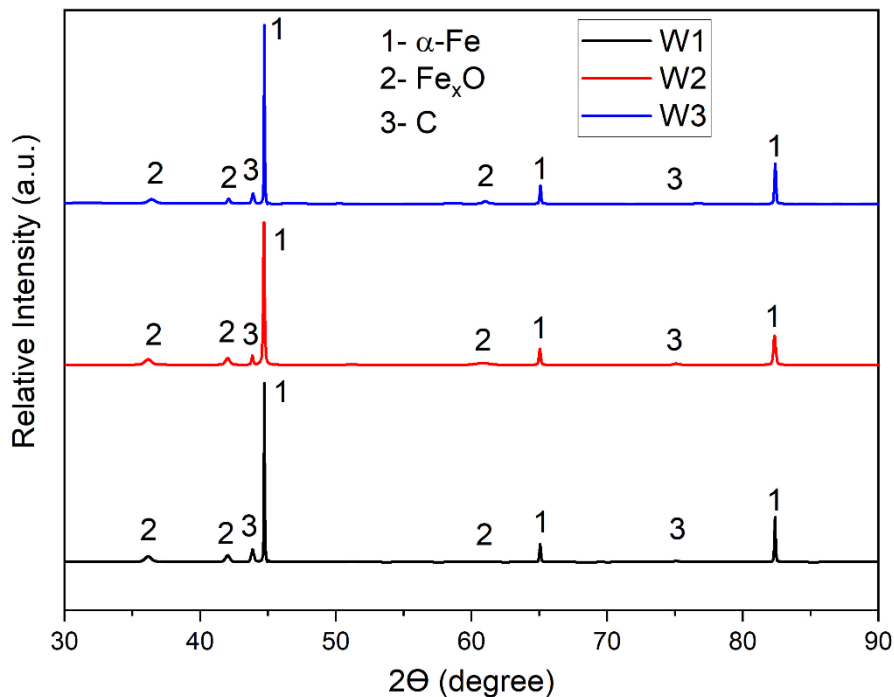


Figure 4.8 X-ray diffraction plots for iron ore composite pellets with W1, W2 and W3 charcoals at a reduction temperature of 1000 °C and reduction duration of 30 min.

4.3.4 Reduction Kinetics

Researchers have developed various models to analyse and extrapolate the experimental data on the composite pellet reduction [88, 168-170]. There are two popular first-order models for gas-solid systems: the progressive conversion model (PCM) and the shrinking core model (SCM). The PCM assumes that the reaction occurs throughout the particle at all times with different rates at different places. The SCM assumes that the reaction starts from the outer surface of particles and progresses towards the core, leaving the solid product behind. Over time, it was observed that SCM fits better to the experimental data. Researchers further identified various steps involved in the reaction of the gas-solid systems, which could control or limit the overall reaction. These resistances are i) gaseous reactant diffusion via the gas film layer surrounding the solid., ii) gaseous reactant diffusion through the solid product layer around the unreacted solid, and iii) chemical reaction between gas and solid. Availability of the reactant gas can be additional resistance in the case of composite pellets. These resistances can solely control the overall gas-solid reaction, or they act consecutively and are all linear with the concentration [191]. Equations were developed considering these resistances for gas-solid reactions.

Equations 4.3, 4.4 and 4.5 are model equations widely used to fit iron ore reduction data [168, 192, 193]. Equations use two input parameters: fraction reacted (f), which is defined as the ratio of the extent of reaction at time t to the extent at 30 min. Equation 4.3 assumes that the composite pellet system is isothermal and the carbon gasification is the rate-controlling step during the reduction process. Equation 4.4 assumes that reduction takes place only on the iron ore particles' surface and the unreacted core is separated from reducing gases by a porous product layer. As reduction occurs, the unreacted core shrinks and chemical reaction is assumed to be the controlling step. Equation 4.5 assumes that the diffusion of reducing gases through the product layer is the rate-controlling step.

$$-\ln(1 - f) = kt \quad (4.3)$$

$$1 - (1 - f)^{1/3} = kt \quad (4.4)$$

$$1 - \frac{2}{3}f - (1 - f)^{2/3} = kt \quad (4.5)$$

where, f = fraction reacted at time t , k = rate constant (s^{-1}).

The fitting of the selected models to the experimental data for iron ore charcoal composite pellets at different reduction temperatures are shown in Figure 4.9. Models corresponding to W1, W2 and W3 charcoals are shown in (a, b, c); (d, e, f); and (g, h, i) in Figure 4.9. Researchers classified that the direct reduction phenomena of composite pellets consist of three regimes [168]. In the first regime, CO and H₂ are rapidly produced from charcoal by cracking volatiles. This regime begins with composite pellets being exposed to the reduction temperature and lasts for almost 5 min, as shown in Figure 4.6. Reduction in this regime is the fastest; that is why it is discarded from the kinetic analysis plots in Figure 4.9, plotted from 5 min onwards. As CO changes to CO₂ after reducing the iron ore, the latter combines with the carbon from charcoal to form CO, known as the solution loss reaction. In the second regime, the solution loss reaction is catalysed by iron, as indicated by the initial steep slope in Figure 4.9 [168]. The third regime begins when all of the iron is utilized as catalyst, and reduction proceeds at a slower rate, as is clear from a declining slope towards the second half of the reduction reaction in Figure 4.9 [179].

The diffusion-controlled model (Equation 4.5) best fits the experimental data in every case (i.e., W1, W2 and W3 charcoals), as evident from Figure 4.9. The overall reduction of iron ore charcoal composite pellet is controlled by the diffusion of reducing gases through the solid product layer. Further, in case of W1 charcoal, at higher reduction duration chemical reaction model fits slightly better. Hu et al. also reported the iron ore charcoal reduction process to be

diffusion controlled [181]. In the case of iron ore composite pellets using coal as a reductant, some authors [168, 179, 180] suggested that coal gasification or solution loss reaction controlled the overall reduction reaction. The gasification step was not found to be the rate-controlling step in the present study, possibly because the kinetics of charcoal gasification is faster than coal [88, 179]. Models fit relatively better to W2 ($R^2=0.95-0.99$) and W3 ($0.95-0.99$) than W1 ($0.89-0.99$) charcoal.

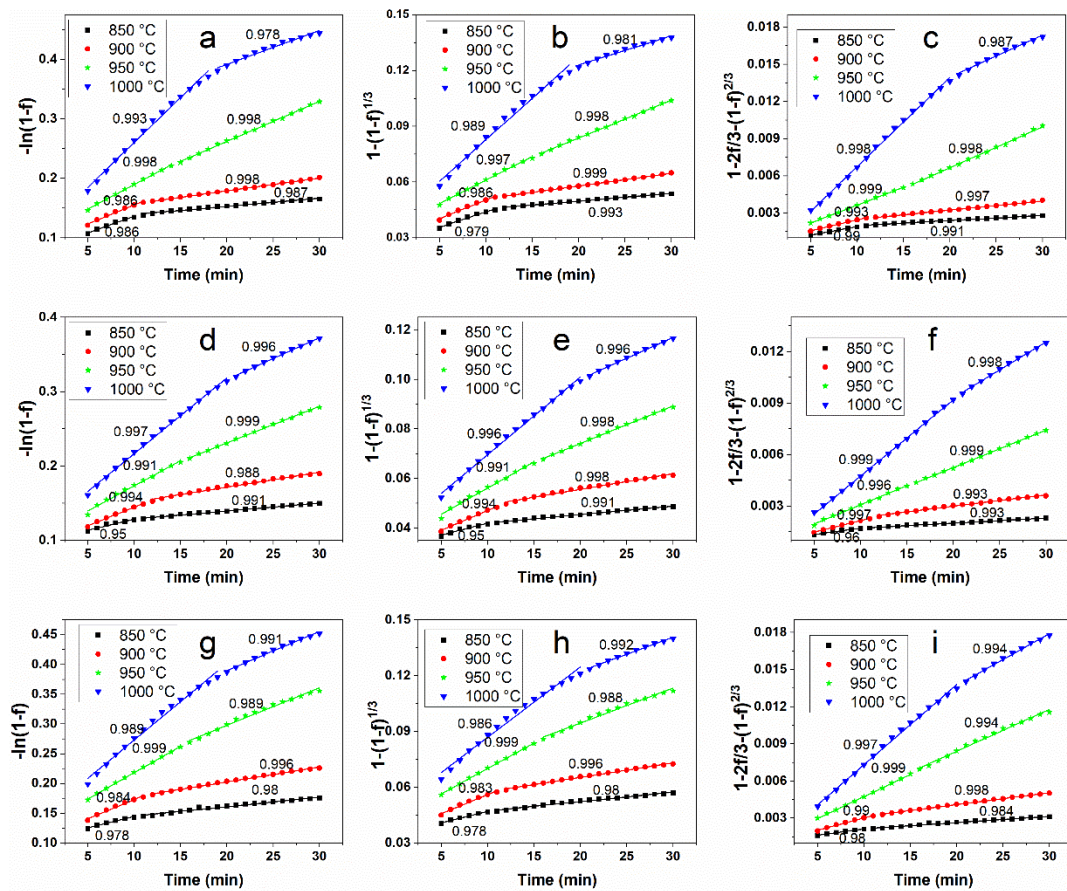


Figure 4.9 Fitting of the selected models to the experimental data for iron ore charcoal composite pellets with W1 (a, b and c), W2 (d, e and f) and W3 (g, h and i) charcoals at different reduction temperatures.

The average slopes from the best fit model were selected to plot $\ln(k)$ vs. $10^4/T$ plot shown in Figure 4.10 (equation 4.6). The slope of the plot equates to E_a/R , where E_a is activation energy and R is gas constant. Apparent activation energies calculated from Equation 4.7, are listed in Table 4.2. The activation energy of finite bed dimension that is being calculated here includes the effect of heat and mass transfer on the overall kinetics. Therefore, activation energy is being

termed as “apparent activation energy”. Calculated activation energies are in range with the previously reported values [169, 170]. W3 (170 kJ/mol) had the lowest activation energy and W2 (213 kJ/mol) the highest. The variation in these values indicate that some other mechanism is also there along with the diffusion control. Small iron ore particles were impervious to reducing gas and resistance to the diffusion of gaseous reactant through the solid product layer was the rate-controlling step. However, it can be seen from Figure 4.7 that the product DRI is porous, which offers lesser resistance to the diffusion of reactant gases and also, the rate of CO generation dwindles over time. It is quite possible that gasification of charcoal or availability of CO became the rate-controlling step subsequent to the diffusion.

$$k = Ae^{\left(\frac{-E_a}{RT}\right)} \quad (4.6)$$

$$m = -\frac{E_a}{R} \quad (4.7)$$

where, k = Chemical reaction rate coefficient, A = Pre-exponential factor, E_a = Activation Energy, R = Gas constant, T = Temperature in °C, m = slope.

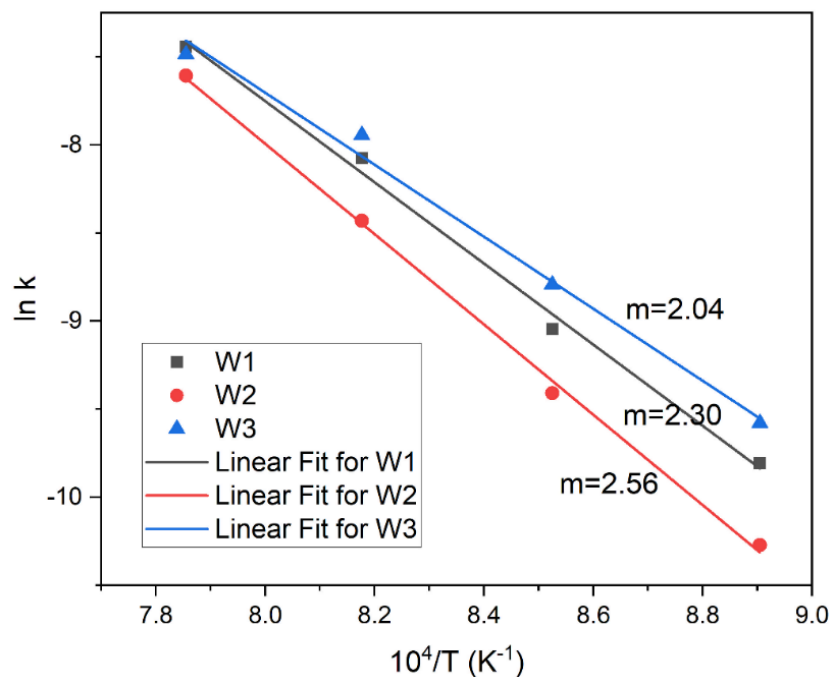


Figure 4.10 ln(k) vs $10^4/T$ plot for iron ore charcoal composite pellets.

Table 4.2 Apparent activation energies for the reduction of iron ore with W1, W2 and W3 charcoal composite pellets.

Charcoal Species	W1	W2	W3
Activation energy(kJ/mol)	191.5±5	213.2±3	169.94±4

4.4 Conclusions

Iron ore-charcoal composite pellets were isothermally reduced in a nitrogen atmosphere at different temperatures for 30 min. The operating parameters such as C/O ratio, reduction temperature and durations were optimized. Charcoals from three fast-growing, hardwood species carbonized at three different temperatures served as a fuel and as a reductant in the composite pellets. A kinetic study was performed using three popular models for the reduction of composite pellets. Following conclusions were drawn from the study:

1. 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 carbonized at a temperature of 800 °C yielded the highest %R, due potentially to a higher reactivity of the carbon towards CO₂.
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.
3. The apparent 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.

4. Charcoals are more reactive as reductant than non-renewable coal. Charcoals are CO₂-neutral, which makes charcoals more environmentally friendly. These properties make charcoals better replacement to coal in ironmaking via the reduction of composite pellets. Results from reduction tests suggested that among the selected biomasses, *Acacia* (W1) and *Leucaena* (W3) are better reductants than *Albizia* (W2) charcoal.