CHAPTER 5

RESULTS AND DISCUSSION ON TG - DTA

This chapter deals with the analysis of experimental data generated on thermogravimetric and differential thermal analysis (TG-DTA) of coals and ore-coal composite pellets in accordance with the scheme of experiments presented in chapter 4 and subsequently presents the results and discussion on non-isothermal reduction studies of ore-coal composite pellets.

5.1 Introduction to Thermal Analysis

Thermogravimetric analysis or thermogravimetry (TG) is used to determine changes in sample weight, which may result from chemical or physical transformations, as a function of temperature or time. The sample may either lose weight to the atmosphere or gain weight by reaction with the atmosphere. TG record is generally in the form of an integral curve, with absolute weight (W) as the Y-axis and time (t) or temperature (T) as the X-axis. The shape of the TG curve is influenced by several factors; the most important being heating rate, sample, and atmosphere [175]. The data obtained provides information concerning the thermal stability and decomposition behaviour of the original sample. Derivative thermogravimetric analysis (DTGA) involves the measurement of the rate of change in weight of a sample as the temperature is increased at a predetermined rate. This technique gives information on the overall weight change for a material, but does not provide information about the nature of products evolved and, therefore, an understanding of the decomposition process becomes difficult [174].

Differential thermal analysis (DTA) can be used to detect the physical and chemical changes, which are accompanied by a gain or loss of heat in a material as a function of temperature or time. It involves heating or cooling of a sample and an inert reference material in close proximity at a linear heating rate as well as monitoring and recording the temperature of the furnace, and the difference in temperature between the sample and the reference material [175]. The differential thermogram consisting of a record of the difference in sample and reference temperature (ΔT) plotted as a function of time (t), sample temperature (T_s), reference temperature (T_r) and furnace temperature (T_f) provide valuable information on phase transitions and chemical reactions. DTA technique is especially suited to studies of structural changes within a solid at elevated temperatures. DTA is capable of giving good qualitative data about the temperatures and indications of transitions. TG and DTA are often used in conjunction, because they complement each other. A TG-DTA apparatus consists of physical property sensors, controlled furnace atmosphere, temperature programmer and recording devices interfaced to a computer, which oversees the operation of the instrument, temperature control, heating and cooling rate, and storage of data.

5.2 Results and Discussion on Pyrolysis of Coal

The total weight loss during reduction of iron ore-coal composite pellet represents the weight loss due to carbon and volatiles present in coal and oxygen present in iron oxide. Since thermogravimetric analysis of composite pellet does not provide a separate record of removal of volatiles; the pyrolysis of coal was done in inert atmosphere to get idea the evolution of volatiles during reduction of composite pellet.

Coal pyrolysis is an initial step in the coal thermal decomposition process and plays an important role in coal based direct reduction of iron ore. During pyrolysis, the structure of the coal changes and becomes more porous. This increases the rate of production of reductants through the Boudouard reaction ($C + CO_2 \rightarrow 2CO$) and water-gas reaction ($C + H_2O \rightarrow CO + H_2$) and decreases the thermal conductivity of the pellet [176].

The detail of the equipment used for pyrolysis of coal is given in Section 4.6.1. TG-DTA profiles of coals from Jharia mines, Dhanbad and Bhilai Steel Plant, Bhilai are shown in Figures 5.1 and 5.2 respectively and their weight losses during pyrolysis are presented in Table 5.1.

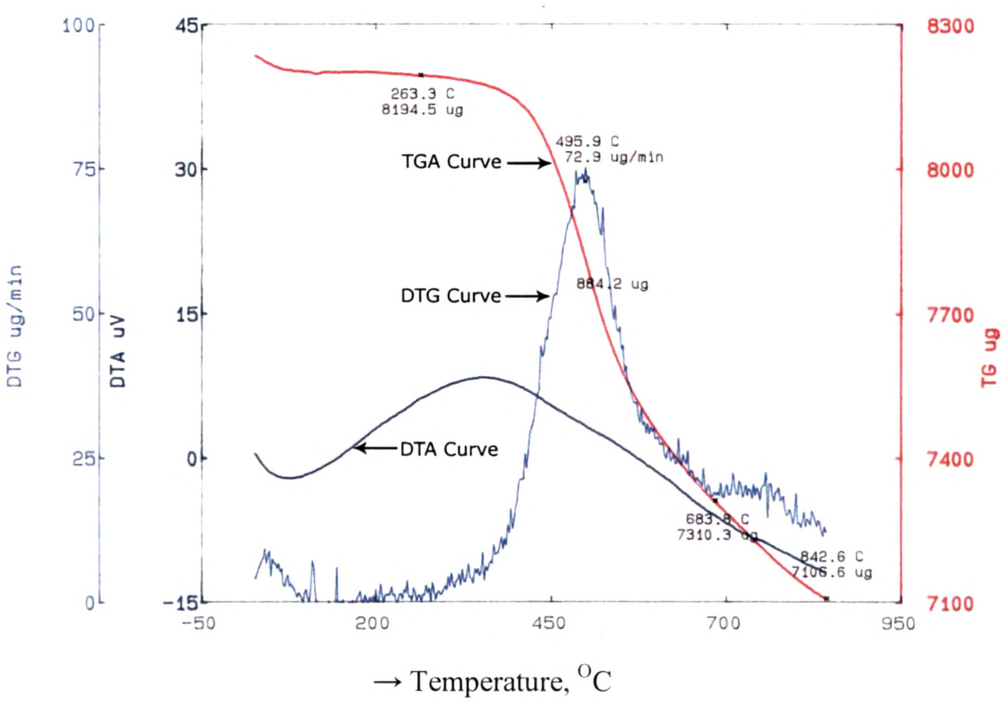


Fig. 5.1: TG-DTA of coal (source: Jharia mines, Dhanbad).

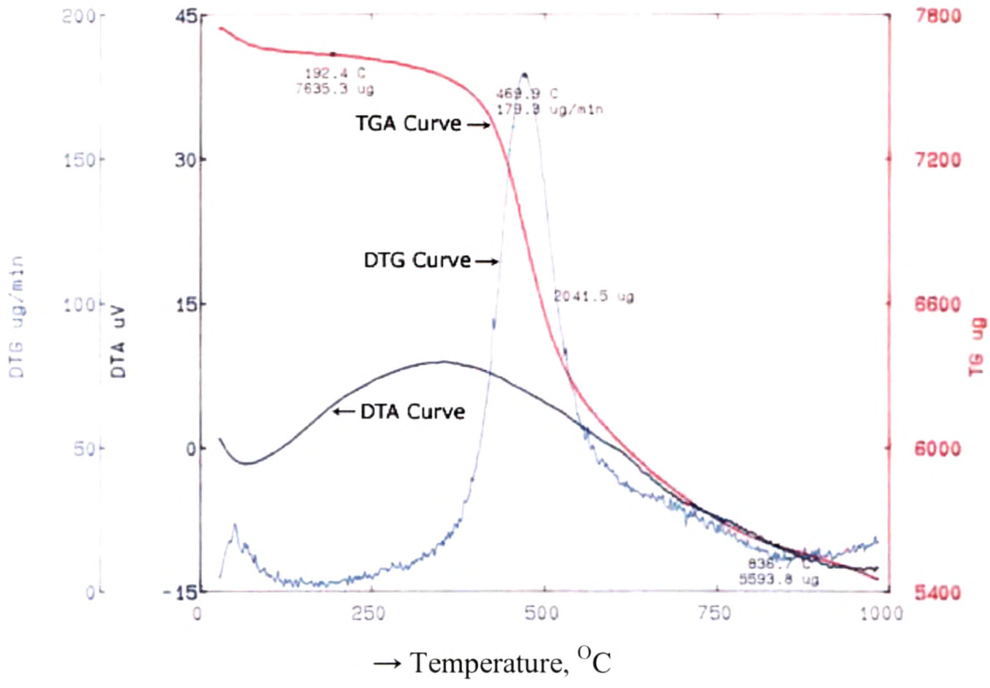


Fig. 5.2: TG-DTA of coal (source: Bhilai Steel Plant, Bhilai).

Table 5.1: Results of TG-DTA for pyrolysis of coal

Conditions:

- Heating rate: 15 K/min
- Crucible: Platinum crucible
- Reference material: Alpha alumina
- For coal from Jharia mines:
  Initial weight of sample: 8231 μg
  Program temperature: 298 to 1223 K
  Actual temperature obtained: 1116 K
- Furnace atmosphere: Argon
  (Ar gas flow rate: 300 cc/min)
- For coal from Bhilai Steel Plant:
  Initial weight of sample: 7753 μg
  Program temperature: 298 to 1273 K
  Actual temperature obtained: 1169 K

Temperature range (^{0}C)	Temperature range (K)	Weight loss (μg)	Weight loss (pct)	Cumulative weight loss (pct)
Coal from Jharia mines				
25.0 - 263.3	298.0 - 536.3	36.5	0.44	0.44
263.3 - 683.8	536.3 - 956.8	884.2	10.74	11.18
683.8 - 842.6	956.8 - 1115.6	203.7	2.48	13.66
Coal from Bhilai Steel Plant				
25.0 - 192.4	298.0 - 465.4	117.7	1.52	1.52
192.4 - 836.7	465.4 - 1109.7	2041.5	26.33	27.85
836.7 - 896.0	1109.7- 1169.0	47.4	0.61	28.46

For coal sample from Jharia mines, there are three temperature ranges to consider (as shown in Figure 5.1). (i) Below 536.3 K, the coal loses its moisture, (ii) between 536.3 and 956.8 K, the weight loss is significant because of tar and volatile release, and (iii) above 956.8 K, the weight loss is small as only gases are released.

i) The initial weight loss (0.44 pct of initial coal weight) observed at temperatures 536.3 K represents the loss of moisture. It is reported in the literature [28b] that most of the uncombined water is driven-off below 375 K. However, for complete removal of uncombined water, temperature up to 575 K is required.

ii) The major weight loss (10.74 pct), occurred between 536.3 and 956.8 K, is due to devolatilization of coal. In this temperature range the weight loss is very rapid as evident from the DTG profile. It was reported [49] that from 623 to 873 K, light gases of CO, CO_2, H_2, CH_4 and C_2H_6 are evolved. Above 873 K, small amounts of complex hydrocarbons are observed. Patisson et al [28a] also studied the pyrolysis of coal in the temperature range of 293 to 1123 K in inert atmosphere. The exit gases were analyzed by gas chromatograph. The exit gases consisted of the composition in C_2H_4, C_2H_6, C_2H_2, CO_2, CH_4, CO and H_2.

iii) Between 956.8 and 1115.6 K, only 2.5 pct weight loss occurred. This may be attributed to high temperature pyrolysis of coal [28b, 177]. The total weight loss (13.66 pct) here is slightly lower than that of the volatile matters content (15.65 pct) of coal as obtained in proximate analysis (Table 4.5). This is due to incomplete removal of volatiles as the overall pyrolysis temperature was low.

It was also reported in literatures [28b, 30] that during the coal pyrolysis, hydrogen evolution takes place at around 1050 to 1100 K. But Dutta and Ghosh [27] observed hydrogen peaks at around 750 to 850 K for their studies on devolatilization of coals. To explain this phenomena (i.e. hydrogen evolution at low temperature), they reported that this is due to reaction of carbon with moisture ($C + H_2O = CO + H_2$). It was also observed [28a] that compared to the coke oven gas, the volatile species produced differed by a high H_2 content and a low CH_4 content, due to more extensive cracking of methane ($CH_4 = C + 2H_2$), associated with the more rapid heating rate.

Similar trend was observed for coal sample from Bhilai Steel Plant but with different amount of weight loss (Figure 5.2). (i) The initial weight loss (1.52 pct of initial coal weight) observed at temperatures 465.4 K represents the loss of moisture. (ii) The major weight loss (26.33 pct) occurred between 465.4 and 1109.7 K is due to devolatilization of coal. (iii) Between 1109.7 and 1169 K, only 0.61 pct weight loss occurred. The total weight loss (28.46 pct) here is slightly higher than that of the volatile matters content (27 pct) of coal as obtained in proximate analysis (Table 4.5). This is due to the loss of moisture, which was present in pellet, during pyrolysis.

From TG plots, as shown in Figures 5.1 and 5.2, the weight loss of coal during pyrolysis at an interval of 25 K was also noted and the same is presented in Appendix 5A.

5.3 Results and Discussion on Iron Ore-Coal Composite Pellets

The procedure and variables for non-isothermal reduction studies of iron ore-coal composite pellets is given in Section 4.6.2. Weight loss method was used to determine the degree of reduction for composite pellets. The results of thermal analysis for ACP1 and BCP1 pellets are shown in Figures 5.3 and 5.4 respectively as simultaneous analysis curves (TG, DTG and DTA). The weight loss and degree of reduction for ACP1 and BCP1 pellets during non-isothermal reduction are presented in Table 5.2. In present investigation, Eq. (3.81) is used to calculate the degree of reduction of composite pellets.

The weight loss values presented in Table 5.2 against different temperature ranges are calculated from the TG profile of Figures 5.3 and 5.4 respectively. The sample loses weight in multi-stages, which is evident from the TG weight loss steps and corresponding DTG peaks. The cumulative weight loss represents the weight loss due to the loss of oxygen present in iron oxide and carbon and volatiles present in coal. For ACP1 pellet, the initial weight loss (1.45 pct of sample weight) up to 429.7 K is due to the loss of moisture. Between 429.7 and 1052.6 K, the weight loss is 13.91 pct of the initial weight, which is significantly due to the release of coal volatiles and reduction of iron oxide by hydrogen mainly. In the temperature range of 1052.6 and 1361.3 K, the TG curve shows very rapid weight loss (14.48 pct of the initial weight), which is due to the dominant role of CO in the reduction of iron oxide at high temperature. The DTG profile shows that even at 1361.3 K the reduction is not completed, which may be attributed to the lower reduction temperature. Here, it is pertinent to mention that the degree of reduction will go further up if the reduction temperature is kept higher (up to 1500 K). The broad endotherm observed at temperatures lower than 429.7 K on DTA curve represents the loss of moisture. The second endotherm is observed at 687.4 K, which may be due to the formation of a metaplastic system i.e. mainly release of tar. It was reported in literatures [28b, 178] that below 600 K, endothermic peak was observed due to the evolution of moisture (drying) and primary devolatilization. All these processes (drying and primary devolatilization) are endothermic in nature.

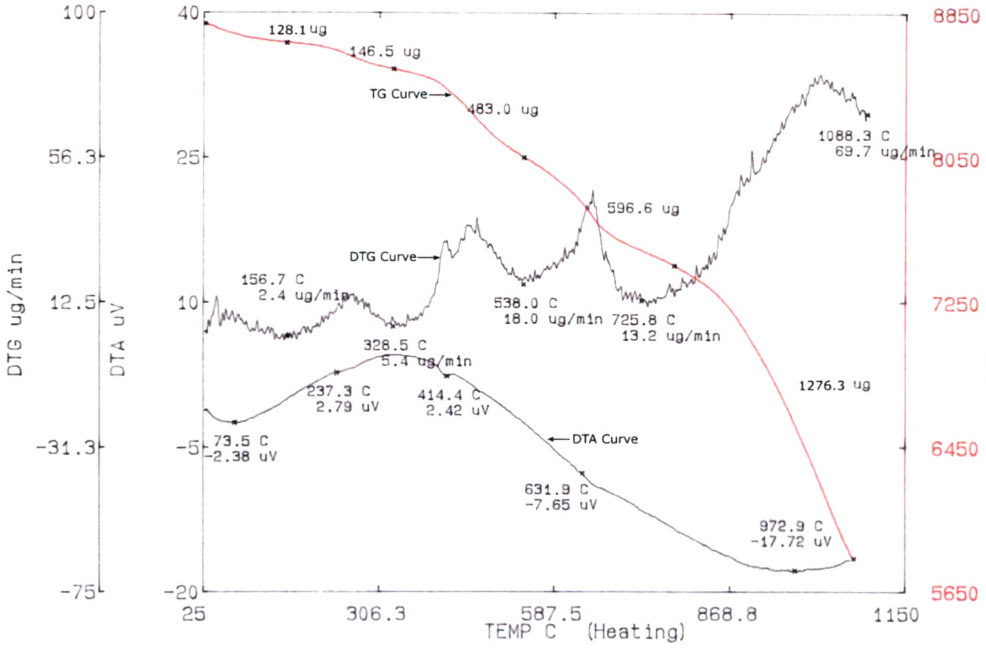


Fig. 5.3: Simultaneous thermal analysis of ACP-1 composite pellet.

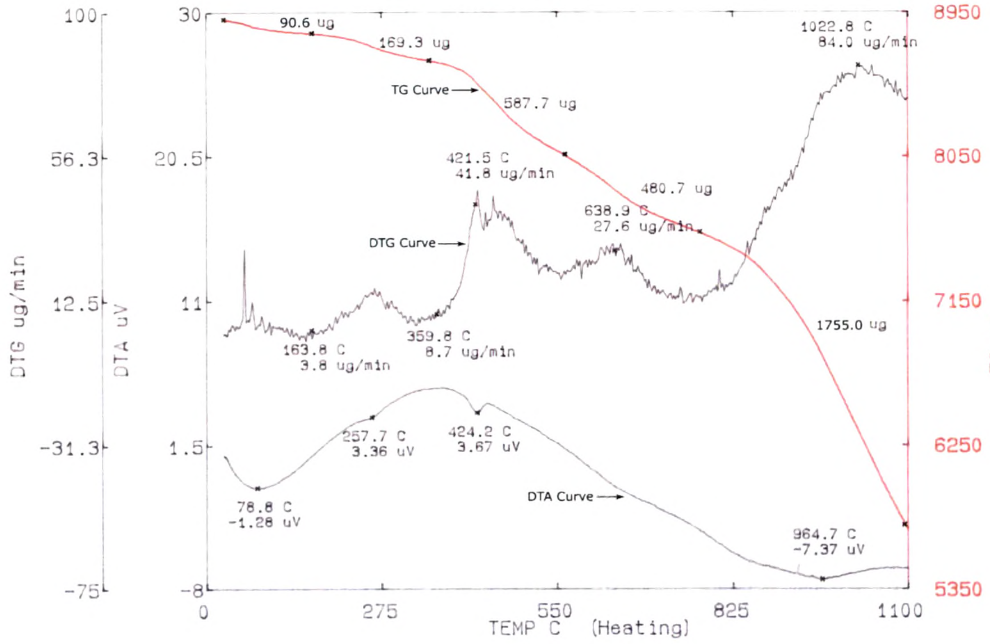


Fig. 5.4: Simultaneous thermal analysis of BCP-1 composite pellet.

Table 5.2: TG results for composite pellets

Conditions:

- Heating rate: 10 K/min
- Crucible: Platinum crucible
- Program temperature: 298 to 1473K
- Actual temperature obtained: 1361 K
- For ACP1 Pellet:
  Initial weight of sample: 8813 μg
- Furnace atmosphere: Argon
  (Ar gas flow rate: 300 cc/min)
- Reference material: Alpha alumina
- For BCP1 Pellet:
  Initial weight of sample: 8910 μg

Temperature range (^{0}C)	Temperature range (K)	Weight loss (μg)	Weight loss (pct)	Cumulative wt loss (pct)	Degree of reduction, α (pct)	Cumult. Degree of reduction, α (pct)
ACP-1 Pellet						
25.0-156.7	298.0-429.7	128.1	1.45	1.45	4.55	4.55
156.7-328.5	429.7-601.5	146.5	1.66	3.11	5.13	9.68
328.5-538.0	601.5-811.0	483.0	5.48	8.59	7.76	17.44
538.0-779.6	811.0-1052.6	596.6	6.77	15.36	16.69	34.13
779.6-1088.3	1052.6-1361.3	1276.3	14.48	29.84	49.93	84.06
BCP-1 Pellet						
25.0-164.9	298.0-437.9	90.6	1.02	1.02	3.18	3.18
164.9-349.5	437.9-622.5	169.3	1.90	2.92	5.01	8.19
349.5-561.1	622.5-834.1	587.7	6.60	9.52	4.81	13.00
561.1-772.7	834.1-1045.7	480.7	5.40	14.92	11.20	24.20
772.7-1087.6	1045.7-1360.6	1755.0	19.70	34.62	62.18	86.38

It was reported [30] that H_2 is available in large quantities for reduction of iron oxides, especially at high temperature, during pyrolysis of the coal. CO is also formed in smaller quantities by pyrolysis but that can be produced by secondary reactions favoured by the temperature increase:

$$C + CO_2 = 2CO \qquad \text{..........(5.1)}$$

$$C + H_2O = CO + H_2 \qquad \text{..........(5.2)}$$

Reaction (5.2) also produces H_2 indicating indirect reduction of iron oxides by the carbon contained in the coal. Sohn and Fruehan [50] observed that weight loss for iron ore-graphite composite pellet reduced by hydrogen gas was much higher than iron ore pellet reduced by only hydrogen. This was due to simultaneous loss of oxygen and carbon during reduction of composite pellet. The possible reducing species in volatiles have been found to be H_2, CO and CH_4, where CH_4 has been cracked to C and H_2 [49].

Dutta and Ghosh [27] found evolution of H_2 at around 1000 to 1100 K for ore-coal composite pellet. This was higher than the temperature range (750 to 850 K) observed in devolatilization of coal. They concluded that reduction of iron oxide by H_2 became significant only above 850 K. Cypres and Moinet [29, 30] also observed that the evolution of hydrogen was significant above 873 K with a maximum at 1073 K and played an important role in the reduction of iron oxides in this temperature range. Therefore, between 873 and 1073 K, the weight loss was partly due to secondary devolatilization of coal and partly due to reduction of magnetite into wustite by hydrogen. Up to about 1073 K, the rate of reduction by H_2 is more rapid than by CO. Around 1073 K, wustite reached its maximum percentage and thereafter it rapidly reduced to iron. From the analysis of gases evolved in TG experiments, they observed that with increase in temperature the significance of CO in the reduction also increases. The CO was formed in smaller quantities by pyrolysis but can be produced by carbon-gasification reaction [Eq. (5.1)] favoured by the increase in temperature. Between 1173 and 1273 K, CO played more dominant role in reduction than hydrogen and the weight loss was due to reduction of wustite into iron.

Similar trend was observed for BCP1 pellet but with different amount of weight loss which is due to the coal having low ash and high volatile matter content. The initial weight loss (1.02 pct of sample weight) up to 437.9 K is due to the loss of moisture. Between 437.9 and 1045.7 K, the weight loss is 13.90 pct of the initial weight, which is significantly due to the release of coal volatiles and reduction of iron oxide by hydrogen mainly. In the temperature range of 1045.7 and 1360.6 K, the weight loss (19.70 pct of the initial weight) is large with rapid rate as indicated by the peak corresponding to 1295.8 K on DTG curve, which is due to the dominant role of CO in the reduction of iron oxide at high temperature. Here also, the DTG profile shows that even at 1360.6 K the reduction is not completed which may be attributed to the lower reduction temperature.

5.3.1 Degree of reduction for composite pellet

A comprehensively review of different methods, used by investigators in past, for measurement of degree of reduction in composite pellets is given in Section 3.5.1. In present investigation, Eq. (3.81), as given below, is used to calculate the degree of reduction for composite pellets.

$$\alpha = \frac{400}{7} \times \left[\frac{f_{wl} - (f_{coal} \times f_{vm} \times f_{vr})}{(f_{ore} \times \rho_{ore} \times f_o)} \right] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.81)$$

Where, f_{wl} = Fractional weight loss = (weight loss of sample / initial weight of sample),

f_{coal} = Fraction of coal present in composite pellet

f_{vm} = Fraction of volatile matters present in coal

f_{vr} = Fraction of volatiles released during reduction at a particular temperature

f_{ore} = Fraction of ore present in composite pellet

ρ_{ore} = Purity of iron oxide (Fe_2O_3)

f_o = Fraction of oxygen present in Fe_2O_3

Method for calculation of f_{vr}: The amount of volatiles released (W_{cvm}) at different temperatures during pyrolysis of coal can be known from the weight loss data for thermogravimetric analysis of coal. Then a factor of proportionality (f_P), representing the ratio of total amount of volatiles present in coal of composite pellet to the total amount of volatiles present in coal sample used for pyrolysis at a particular temperature, was determined. Using the values of W_{cvm} and f_P, the amount of volatiles released (W_{pvm}) at different temperatures during TG-DTA of composite pellet can be calculated. Now, the f_{vr} can be calculated by dividing the W_{pvm} values by the total amount of volatiles present in coal of composite pellet. The factor of proportionality (f_P) varies with source of the coal and the Fe_{tot}/C_{fix} ratio of composite pellet and so the f_{vr} also changes accordingly.

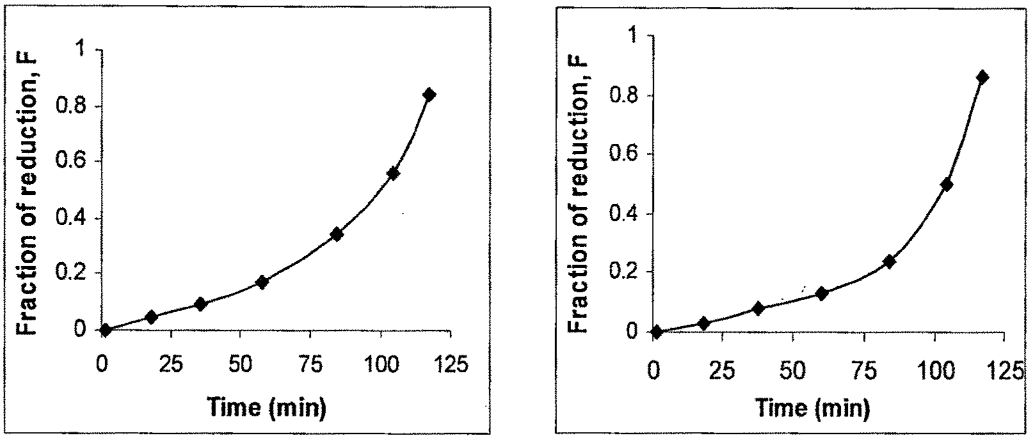
The fraction of volatiles released (f_{vr}) during reduction of composite pellet is calculated using the data presented in Appendix 5A and the values are presented in Table 5.3. Calculation for the fraction of volatiles released (f_{vr}) from composite pellet during TG analysis is shown in Appendix 5B.

Table 5.3: TG results for non-isothermal reduction of composite pellets

Time (min)	Temp (^{0}C)	Temp (K)	Wt. loss (μg) wrt initial weight	Fractional wt. loss, (f_{wl} x10^2)	Amt. of VM released (μg)	Fraction of VM released (f_{vr})	Fraction of Reduction, F x10^2	Rate of Reduction, kx10^5(s^{-1})
ACP-1 Pellet								
1.5	27.9	300.9	6.6	0.075	Nil	Nil	0.254	2.82
17.8	156.7	429.6	128.1	1.454	10.05	0.022	4.55	4.26
35.6	328.5	601.5	274.6	3.116	23.25	0.052	9.68	4.53
57.7	538.0	811.0	707.6	8.030	255.12	0.569	17.44	5.04
84.4	779.6	1052.6	1254.1	14.23	368.49	0.822	34.12	6.74
104.1	959.4	1232.4	1826.3	20.72	448.11	1.0	53.07	8.50
117.4	1088.3	1361.3	2630.4	29.84	448.11	1.0	84.06	11.90
ACP-2 Pellet								
1.5	27.9	300.6	7.0	0.084	Nil	Nil	0.267	2.97
17.8	156.8	429.8	90.4	1.08	8.17	0.022	3.13	2.93
38.7	358.1	631.1	242.7	2.91	23.61	0.065	8.35	3.60
61.9	575.5	848.5	556.1	6.67	230.76	0.634	12.39	3.34
79.7	736.6	1009.6	1099.9	13.19	289.26	0.795	30.89	6.46
103.8	954.0	1227.0	1794.7	21.52	364.02	1.0	54.51	8.75
117.4	1085.6	1358.6	2465.0	29.56	364.02	1.0	80.06	11.37
ACP-3 Pellet								
0.80	28.6	301.6	0.60	0.007	Nil	Nil	0.021	0.43
16.1	140.6	413.6	40.3	4.48	7.60	0.021	1.12	1.16
35.9	331.2	604.2	184.4	2.05	20.00	0.056	5.62	2.61
47.2	438.6	711.6	338.8	3.77	65.58	0.182	9.37	3.31
63.1	586.3	859.3	592.9	6.59	233.22	0.648	12.30	3.25
75.6	699.0	972.0	917.7	10.21	275.54	0.766	22.00	4.85
100.9	927.0	1200.0	1593.7	17.73	359.93	1.0	42.30	6.99
111.9	1031.9	1304.9	2267.0	25.21	359.93	1.0	65.30	9.73
117.4	1085.6	1358.6	2546.7	28.32	359.93	1.0	74.90	10.63
ACP-4 Pellet								
1.40	27.9	300.9	2.3	0.028	Nil	Nil	0.083	0.98
16.0	140.6	413.6	49.8	0.60	6.34	0.021	1.56	1.63
32.6	299.0	572.0	165.9	2.00	12.91	0.043	5.50	2.81
37.0	341.9	614.9	189.6	2.29	17.06	0.057	6.20	2.79
45.9	427.0	700.0	306.0	3.69	44.55	0.148	9.40	3.41
63.2	589.0	862.0	552.3	6.66	149.14	0.497	14.49	3.82
78.7	728.5	1001.5	854.6	10.30	236.70	0.789	22.19	4.70
102.0	938.5	1211.5	1348.8	16.26	300.14	1.0	37.68	6.16
112.2	1034.6	1307.6	1875.6	22.61	300.14	1.0	56.61	8.41
117.4	1085.6	1358.6	2101.0	25.33	300.14	1.0	64.71	9.19

BCP-1 Pellet								
1.2	27.1	300.1	2.6	0.029	Nil	Nil	0.094	1.31
18.5	164.9	437.9	90.6	1.02	3.13	0.0045	3.18	2.86
37.7	349.5	622.5	259.9	2.92	33.99	0.0487	8.19	3.42
60.2	561.1	834.1	847.6	9.52	489.24	0.701	13.00	3.60
83.6	772.7	1045.7	1328.3	14.92	659.90	0.946	24.20	4.82
104.4	964.7	1237.7	2082.2	23.38	697.41	1.0	50.14	8.00
117.4	1087.6	1360.6	3083.3	34.62	697.41	1.0	86.38	12.30
BCP-2 Pellet								
1.1	27.9	300.9	1.90	0.022	Nil	Nil	0.066	1.00
18.4	162.1	435.1	78.10	0.89	2.51	0.0043	2.62	2.37
34.5	317.8	590.8	195.70	2.23	19.99	0.0342	6.09	2.94
58.9	548.7	821.7	556.70	6.35	402.06	0.688	14.30	4.05
82.5	763.5	1036.5	1133.30	12.93	549.36	0.940	20.30	4.10
103.6	954.0	1227.0	1942.9	22.17	584.71	1.0	47.16	7.58
117.4	1088.3	1361.3	2986.9	34.08	584.71	1.0	83.40	11.83
BCP-3 Pellet								
1.2	27.9	300.9	5.4	0.062	Nil	Nil	0.183	2.54
19.2	170.2	443.2	92.3	1.06	2.39	0.0045	3.06	2.66
38.6	358.1	631.1	249.9	2.86	28.67	0.0539	7.49	3.23
56.6	527.2	800.2	631.8	7.24	331.67	0.624	20.3	5.98
78.1	723.2	996.2	1156.2	13.25	482.10	0.907	22.8	4.87
103.1	948.7	1221.7	1948.9	22.23	531.70	1.0	48.03	7.76
117.4	1085.6	1358.6	2878.8	32.99	531.70	1.0	79.58	11.31
BCP-4 Pellet								
1.6	27.9	300.9	2.6	0.031	Nil	Nil	0.088	0.92
20.8	18306	456.6	90.3	1.06	2.88	0.0062	2.95	2.36
36.4	336.6	609.6	237.3	2.79	19.68	0.0422	7.36	3.36
56.9	529.9	802.9	621.3	7.31	293.56	0.6292	11.09	3.25
79.0	731.2	1004.2	1104.4	12.99	426.27	0.9136	22.93	4.84
103.1	948.7	1221.7	1837.5	21.62	466.57	1.0	46.39	7.50
117.4	1085.6	1358.6	2692.7	31.68	466.57	1.0	75.32	10.70

Figure 5.5 shows fraction of reduction (F) as a function of time for both ACP1 and BCP1 pellets in the temperature range of room temperature to 1361 K. The degree of reduction was increased with time of heating and rise in temperature. For ACP pellet, initially the fraction of reduction was very low which may be due to the release of volatiles, which is very slow process. But later on the fraction of reduction increased with time, which may be attributed to the faster gas-solid reactions at high temperature. Similar trend was also observed for BCP pellet.



(a) (b)

Fig. 5.5: Fraction of reduction *vs* time plot for (a) ACP1 pellet and (b) BCP1 pellet.

Calculation for the degree of reduction for composite pellet according to Eq. (3.81) is shown in Appendix 5C. The degree of reduction for composite pellets of different Fe_{tot}/C_{fix} ratios is presented in Table 5.4.

Table 5.4: Results for final degree of reduction of composite pellets

Conditions:

- Heating rate: 10 K/min
- Crucible: Platinum crucible
- Reference material: Alpha alumina
- Weight of reference material: 8800 μg
- Atmosphere: Argon
- (Ar gas flow rate: 300 cc/min)
- Programmed temperature:298 to1473 K
- Highest temperature obtained: 1361 K

Composite Pellet*	Fe_{tot}/C_{fix} ratio	Porosity (pct)	Initial weight of sample (μg)	Total weight loss (μg)	Weight loss (pct)	Degree of reduction, α (pct)
ACP-1	2.50	24.86	8813	2630.4	29.84	84.06
ACP-2	3.11	22.65	8340	2465.0	29.56	80.06
ACP-3	3.50	17.40	8991	2546.7	28.32	74.90
ACP-4	4.00	15.70	8295	2101.0	25.33	64.71
BCP-1	2.50	23.10	8910	3083.3	34.60	86.38
BCP-2	3.11	18.42	8764	2986.9	34.08	83.40
BCP-3	3.50	16.36	8726	2878.8	32.99	79.58
BCP-4	4.00	13.54	8500	2692.7	31.68	75.32

* ACP refers to the composite pellet made with coal from Jharia mines, Dhanbad, and
* BCP refers to the composite pellet made with coal from Bhilai Steel Plant, Bhilai.

Figure 5.6 shows the change in degree of reduction of pellets with Fe_{tot}/C_{fix} ratio. It was observed that with increase in Fe_{tot}/C_{fix} ratio, the degree of reduction decreased which is attributed to the lesser amount of reductant present in pellets as well as decrease of porosity of the pellets (as shown in Table 5.4).

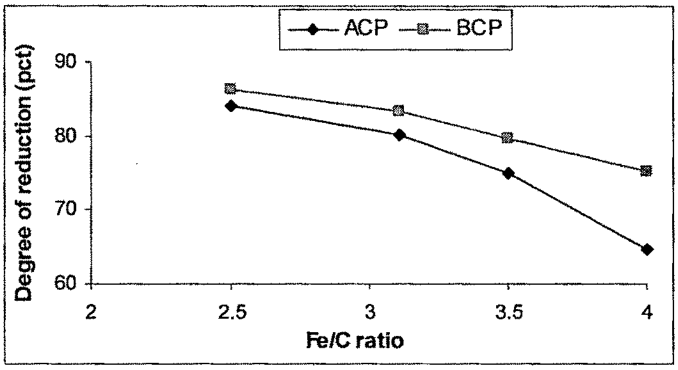
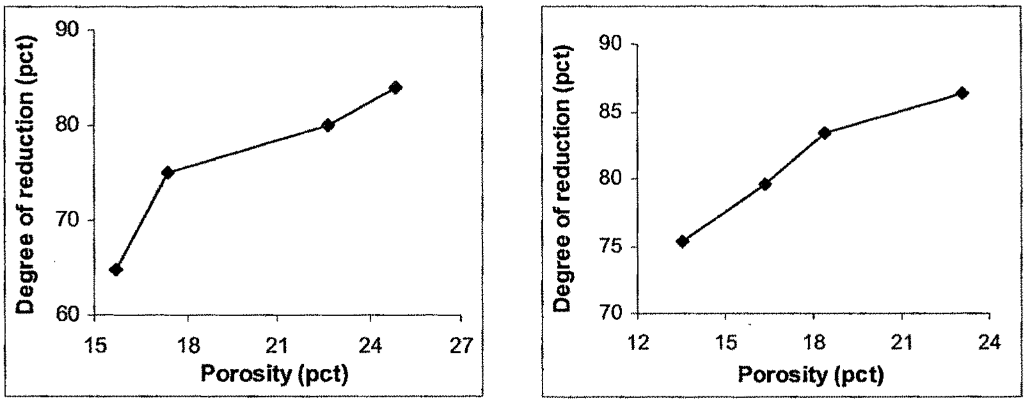


Fig. 5.6: Effect of Fe_{tot}/C_{fix} ratio on degree of reduction of composite pellets.

Figure 5.7 shows the change in degree of reduction of composite pellets with porosity. It was observed that with increase in porosity the degree of reduction also increased which is attributed to larger inner surface area available for reduction. Reduction is rapidly facilitated by the access of reductant, which is available into the interior of the pellet.



(a) (b)

Fig. 5.7: Effect of porosity on degree of reduction of (a) ACP and (b) BCP pellets.

Further, the rise in degree of reduction with increase in porosity of pellet is faster in the beginning and sluggish in later stage. This may be due to the change in porosity as the reduction progresses owing to the removal of oxygen from the oxide lattice, removal of volatiles from coal, volume changes, recrystallization of iron, softening of gangue and sintering of products. Similar results are also reported in literatures [179, 180].

From Table 5.4, it may be noted that:

i) Higher degree of reduction is obtained with Bhilai coal having high volatiles and low ash. The degree of reduction varied in the range of 64 to 84 pct for ACP (coal from Jharia mines) pellets and 75 to 87 pct for BCP (coal from Bhilai steel plant) pellets.

ii) With increase in Fe_{tot}/C_{fix} ratio, the degree of reduction decreased which is due to the lesser amount of reductant present in the composite pellet (as shown in Figure 5.6).

iii) For the same Fe_{tot}/C_{fix} ratio of two different types of pellets, it is observed that coal with high volatile matters resulted in higher degree of reduction. Similar observations were also reported in the literature [37, 43].

Further, final degree of reduction for composite pellets (α) was calculated using following equations (given in Section 3.5.1) and is presented in Table 5.5 so as to have a comparison among these methods.

i) According to Eq. (3.64) used by Yang et al [164]:

$$\alpha = \frac{(W_0 - W_f)\times 100}{W_0 \times \left(\frac{3M_{CO}}{M_{Fe_2O_3} + 3M_C}\right)} \qquad \text{............(3.64)}$$

ii) According to Eq. (3.65) used by Chowdhury et al [165]:

$$\alpha = \frac{\frac{32}{44}\times W_r}{f_o \times W_h} \qquad \text{............(3.65)}$$

iii) According to Eq. (3.81) which is a modified equation of Wang et al [43]:

$$\alpha = \frac{400}{7}\times\left[\frac{f_{wl} - (f_{coal}\times f_{vm}\times f_{vr})}{(f_{ore}\times \rho_{ore}\times f_o)}\right] \qquad \text{............(3.81)}$$

From Table 5.5 it may be observed that the degree of reduction (α) values, for the same Fe_{tot}/C_{fix} ratio, shows a significant difference by calculation. Since Yang et al [164] used graphite as reductant with the assumption that the total amount of reduction of iron oxides by CO is equal to the amount of the carbon solution loss reaction. Chowdhury et al [165] used iron ore-graphite composite pellets for their study; assuming no CO in the exit gas and neglecting any volatile loss. The degree of reduction was estimated through weight loss and corresponding gas analysis. For many pellets, the α values are more than 100 pct which looks absurd and may be due to neglecting the volatile loss. Wang et al [42] reported that for reduction of 16-18 mm diameter pellets, at temperatures less than 1173 K, the effect of volatiles is significant, but at higher temperatures (more than 1323) they [43] reported that effect of volatiles is negligible.

Table 5.5: Comparison of final degree of reduction for composite pellets

Composite Pellet	Fe_{tot}/C_{fix} ratio	Degree of reduction, α (pct) [as per Eq. 3.64]	Degree of reduction, α (pct) [as per Eq. 3.65]	Degree of reduction, α (pct) [as per Eq. 3.81]
ACP-1	2.50	69.64	107.00	84.06
ACP-2	3.11	68.96	101.90	80.06
ACP-3	3.50	66.09	95.34	74.90
ACP-4	4.00	59.10	82.40	64.71
BCP-1	2.50	80.74	110.00	86.38
BCP-2	3.11	79.52	106.20	83.40
BCP-3	3.50	76.98	101.34	79.58
BCP-4	4.00	73.92	95.89	75.32

Further, the degree of reduction (α) for composite pellets ACP1 and BCP1 having same Fe_{tot}/C_{fix} ratio of 2.50 in stage wise was calculated using Equations (3.76) and (3.81) [given in Section 3.5.1] and is presented in Table 5.6 to have a comparison among these methods. Calculation for degree of reduction of composite pellet, according to Eqs. (3.76) and (3.81), is shown in Appendix 5D.

i) According to Eq. (3.76), original equation developed by Wang et al [43]:

$$\alpha = \frac{4}{7\,m_o}[\Delta m_t - (m \times f_v)] \times 100 \qquad ....(3.76)$$

ii) According to Eq. (3.81), which is a modified equation of Wang et al [43]:

$$\alpha = \frac{400}{7} \times \left[\frac{f_{wl} - (f_{coal} \times f_{vm} \times f_{vr})}{(f_{ore} \times \rho_{ore} \times f_o)} \right] \qquad ....(3.81)$$

Table 5.6: Comparison of degree of reduction for composite pellets

ACP1 Pellet (Fe_{tot}/C_{fix} ratio = 2.50)			BCP1 Pellet (Fe_{tot}/C_{fix} ratio = 2.50)		
Temperature (K)	Degree of reduction, α (pct) [as per Eq. 3.76]	Degree of reduction, α (pct) [as per Eq. 3.81]	Temperature (K)	Degree of reduction, α (pct) [as per Eq. 3.76]	Degree of reduction, α (pct) [as per Eq. 3.81]
601.5		9.68	622.5		8.19
811.0	9.99	17.44	834.1	5.40	13.00
1052.6	31.04	34.12	1045.7	22.85	24.20
1232.4	53.07	53.07	1237.7	50.14	50.14
1361.3	84.06	84.06	1360.6	86.38	86.38

From Table 5.6, it may be noted that for ACP1 pellets at temperatures 601.5, 811 and 1052.6 K the degree of reduction (α) calculated by Wang et al's original Eq. (3.76) and modified Eq. (3.81) differs but at temperatures 1232.4 and 1361.3 K the degree of reduction (α) remains same. Generally, the volatiles in composite pellet get completely released at temperatures below 1173 K and the effective reduction caused by these volatiles makes difference in the values of degree of reduction. It was reported in literatures [30, 42, 43] that at temperatures below 1173 K the effect of volatiles is significant but at temperatures above 1323 K the effect is negligible.

In present investigation, the author used iron ore-coal composite pellets for reduction studies. Eq. (3.81) includes the term f_{vr} (fraction of volatiles released during reduction). The release of volatiles from composite pellet is gradual and occurs over a wide range of temperature. The values of f_{vr} can be calculated at different temperatures as shown in Appendix 5B. The role of volatiles in reduction of iron ore-coal composite is well established [8, 37, 49, 169]. The quantum of volatiles released at different temperatures take part in reduction reactions and therefore, it is more appropriate to use Eq. (3.81) to calculate the degree of reduction for composite pellets. However, Eq. (3.76) does not take into account of the gradual release of volatiles, rather considers the total release of volatiles and therefore, the final degree of reduction remains the same as calculated by Eq. (3.81) but for initial part of reduction the degree of reduction values differ and are less from that calculated by Eq. (3.81). Hence, the degree of reduction calculated by Eq. (3.81) is more accurate than that of Eqs. (3.64), (3.65) and (3.76).

5.4 Kinetic Analysis of Non-isothermal Reduction of Composite Pellets

The reduction kinetic data obtained from TG-DTA of composite pellets are presented in Table 5.3. The rate of reduction, k (s^{-1}) can be obtained by dividing the fraction of reduction (F) by time (s) at a particular temperature.

$$k = F/t \qquad \text{............(5.3)}$$

Arrhenius equation:

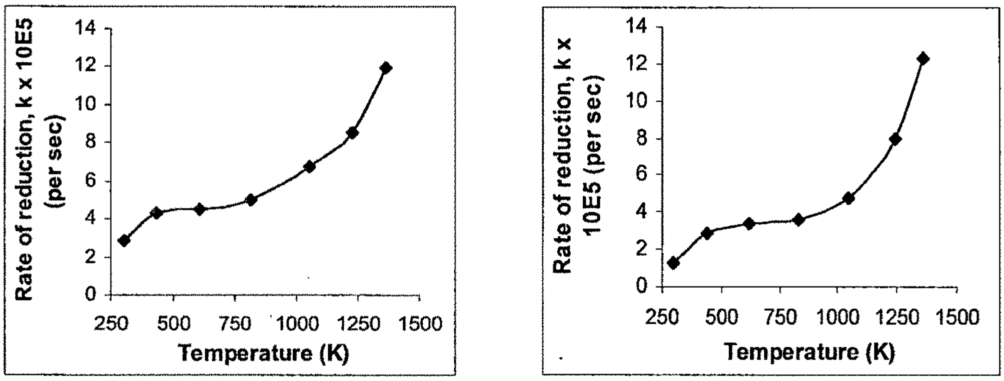
$$k = A \exp(-E/RT) \qquad \text{............(5.4)}$$

Where, A = pre-exponential factor (s^{-1})
E = activation energy ($kJ.mol^{-1}$)
R = gas constant ($kJ.mol^{-1}.K^{-1}$)
T = temperature (K)
k = rate constant (s^{-1})

Taking logarithm on both sides of the equation (5.4) results:

$$\ln k = \ln A - (E/RT) \qquad \text{.............(5.5)}$$

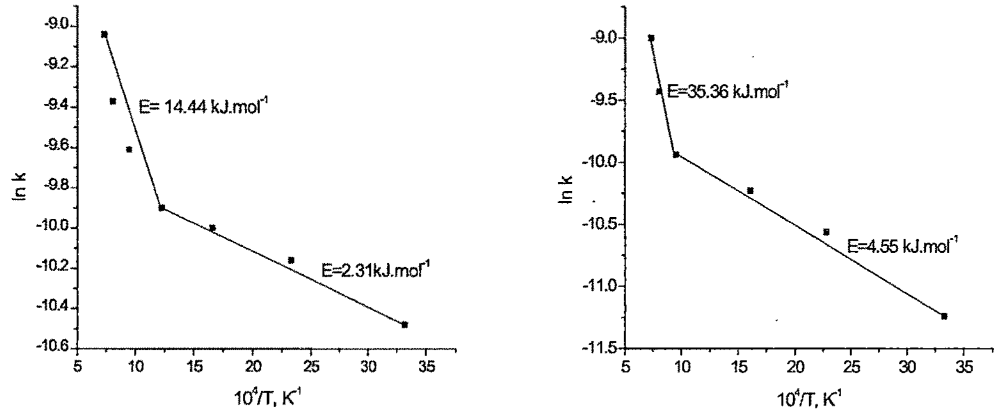
Eq. (5.5) is used in analyzing the reduction kinetic data. A plot of ln k *vs* 1/T gives slope (-E/R) and from the slope of the line, the activation energy (E) can be estimated. The data required for estimation of activation energy (E) are presented in Appendix 5E.



(a) (b)

Fig. 5.8: Rate of reduction *vs* temperature plot for (a) ACP1 and (b) BCP1 pellets.

Figure 5.8 shows that the rate of reduction increases with increase in temperature. The curves can be divided into three segments. Initially (at 301 to 430 K for ACP pellet), rate of reaction is very fast due to rapid release of moisture. After that (at 430 to 811 K), rate becomes very slow, more or less constant. That is due to devolatilization of coal. Finally (at 811 to 1361 K), rate of reduction is again increased with temperature due to rapid gas-solid reactions. It was reported [42] that with increase in temperature from 693 to 993 – 1013 K, the reduction rate by volatiles increased very slowly, but above 993 to 1013 K the reduction rate by volatiles rapidly increased. This indicates that there is a beginning temperature for reduction by volatiles. At later stage, the reduction rate increases due to rapid reduction of iron oxide by CO in the presence of hydrogen [179].



(a) (b)

Fig. 5.9: Arrhenius plot for non-isothermal reduction of composite pellets (a) ACP1 and (b) BCP1.

The activation energy (E) values calculated for composite pellets of different Fe_{tot}/C_{fix} ratios are presented in Appendix 5E and Arrhenius plots for ACP1 and BCP1 pellets are shown in Figure 5.9. The computed values of activation energy are in the range of 0.86 to 8.82 kJ/mol for initial stage of reduction and 12.37 to 38.32 kJ/mol for the later stage of reduction. The given activation energy values indicated that the reduction process at the earlier stages is controlled by gaseous diffusion mechanism. At the final stages, the mixed control reaction mechanism is the rate determining step. The reduction mechanism could be controlled by a combined effect of both gaseous-diffusion and chemical reaction processes. These values are comparable to the values of activation energy reported in the literatures. El-Geassy et al [46] obtained activation energies 18.81 to 28.42 kJ/mol for non-isothermal reduction of composite pellets in N_2 atmosphere. They observed that at early stages, an incubation period was detected and the reduction was controlled by the gaseous diffusion mechanism. Dutta [41] found three stages of reactions for low heating rate (10.5 K/min); the activation energy for stage I was very low (6.1 to 13.2 kJ/mol) due to diffusion of volatile gases to the iron ore particles boundary. In stage II, values of activation energy were 26.4 to 42.5 kJ/mol, which is due to hydrogen gas diffusion through the porous solid. Final stage III activation energy values were 183.1 to 268.5 kJ/mol due to the carbon gasification reaction. Wang et al [43] obtained activation energy 68.95 and 82.61 kJ/mol for iron ore-hard coal (low volatile content) pellet and iron ore-soft coal (high volatile content) pellet respectively. Goswami et al [109] obtained activation energy 60.75 kJ/mol for fluxed composite pellets. They observed a mixed kinetic model where reduction is initially diffusion controlled and later on chemical reaction controlled. Prakash [150] obtained activation energies 1.2 to 14.6 kJ/mol for initial stage and 43 to 46.9 kJ/mol for later stage of reduction by simultaneous thermal analyzer for iron ore-coal mixture under non-isothermal condition.