CHAPTER 5

5.0 GASIFICATION WITH CARBON DIOXIDE: RESULTS AND DISCUSSION

5.1 Introduction

The results of the char-CO_2 gasification experiments are presented in this chapter. The chars were prepared at 900 °C according to a procedure described earlier in Section 3.4.1. The gasification reaction experiments were carried out in the Thermax 500 TGA following the method already discussed in Section 4.4. The main focus of this chapter is: (i) to show the relative impact of the operating conditions (temperature, CO_2 concentrations and different chars) on the carbon conversion; and (ii) to correlate the reactivity results with the properties of the coals and chars as obtained from the detailed characterisation results of Chapter 3.

5.2 Normalisation of the Experimental Results

Results recorded by the TGA are in a format showing the relative loss in mass, time and temperature. A typical experimental result obtained from the TGA is shown in Figure 5.1.

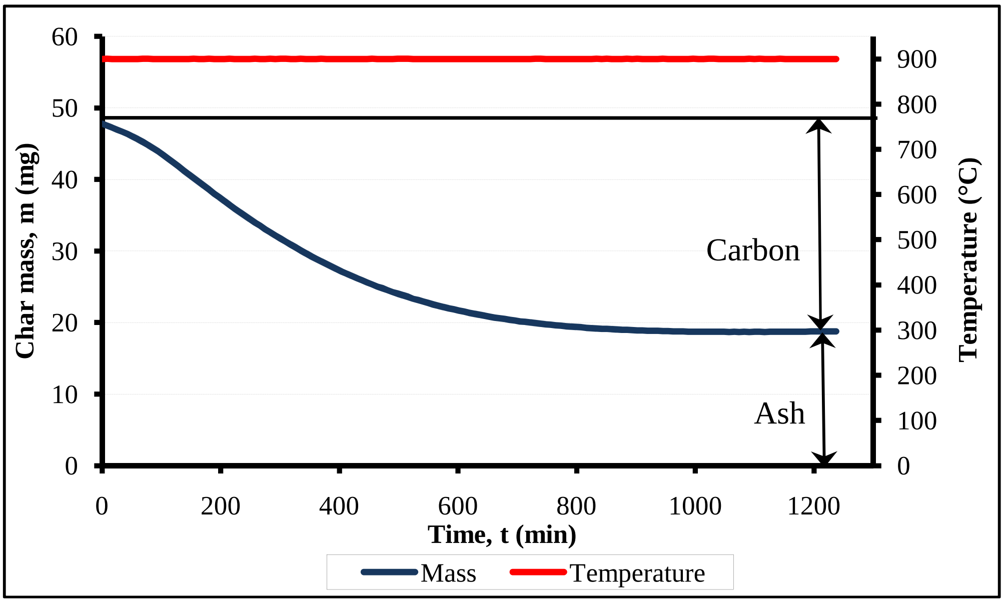


Figure 5.1: Typical mass loss curve for char C2 at 900 °*C*, 100% CO_2, 0.875 *bar*.

A rapid decrease in mass was observed during the initial stage of the reaction until about 50% mass loss. A slower rate of consumption was observed from this point forward, until an equilibrium stage is reached which indicates that all the carbon compounds in the char have fully reacted with CO_2. It was observed that the final equilibrium mass value corresponded well with the ash content of the chars as determined from proximate analysis (Table 3.8, Section 3.7.1). The mass of reacted carbon also corresponded to the fixed carbon value from the proximate analysis. However, a maximum deviation of ± 5% from the ash and fixed carbon percentages was observed in most of the experiments. These slight deviations may be attributed to the heterogeneity of the individual char particles which was not fully eliminated, even with the use of a rotary sample splitter to obtain a representative sample. Furthermore, the unreactive or unreacted highly aromatic parts of the carbon matrix may also introduce some anomalies in the results.

Reaction time for the experiments varied from 12 hours to over 48 hours at lower concentrations of CO_2. Kaitano (2007) also experienced very long reaction time with chars prepared from inertinite-rich low grade coals, similar to chars used in this investigation.

For a quantitative study of the conversion of the fixed carbon in the char only, the TGA raw data were normalised on an ash free basis on the assumption that negligible product gas is produced from mineral transformations or mineral reactions with CO_2 according to Equation 5.1 (Dutta *et al.*, 1977; Hampartsoumian *et al.*, 1993; Kyotani *et al.*, 1993; Ye *et al.*, 1998; Zhang *et al.*, 2006; Çakal *et al.*, 2007; Kaitano, 2007; Zhang *et al.*, 2007; Everson *et al.*, 2006 and 2008a; Wu *et al.*, 2008):

$$X = \frac{m_o - m_t}{m_o - m_{ash}} \tag{5.1}$$

A typical normalized result (carbon conversion versus time plot) from the experimental result of Figure 5.1, is presented in Figure 5.2. The number of data points used throughout this investigation was 29 to 31 and is considered accurate enough for all interpretations as well as for kinetic modelling.

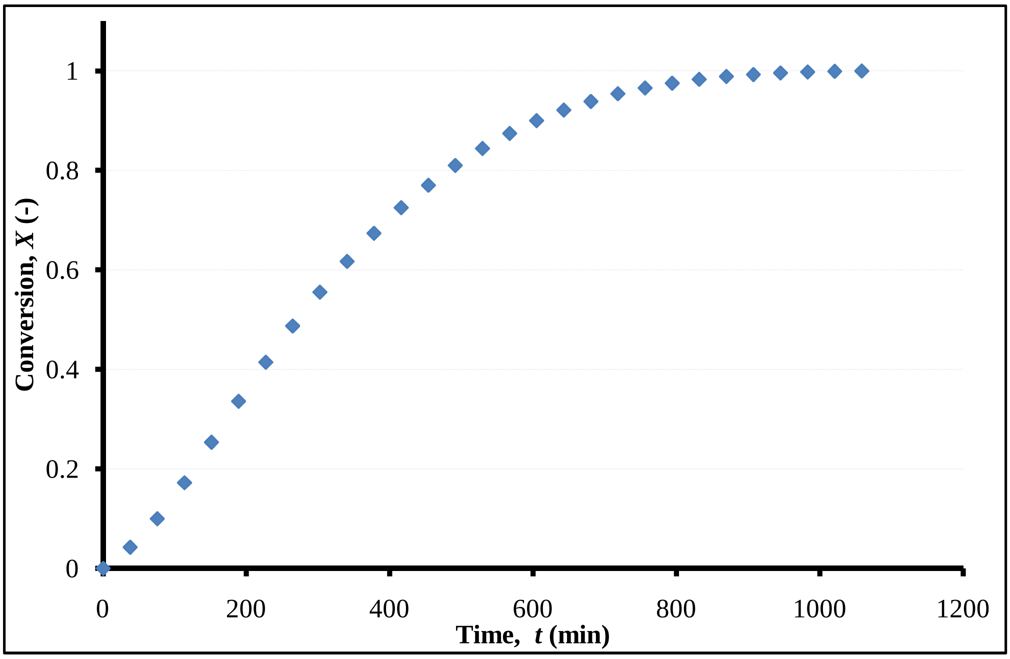


Figure 5.2: Conversion-time plot for char C2 at 900 °C, 100% CO_2, 0.875 *bar*.

5.3 Reproducibility of the Experimental Results

The experimental results from the TGA were crosschecked for reproducibility. This was done by conducting three different experiments with each of the respective char samples at the same operating conditions of temperature and CO_2 concentration. The characteristic experimental data were analysed for initial reactivity, R; structural parameter, ψ; time factor t_f; and time for 50% and 90% conversions ($t_{0.5}$ and $t_{0.9}$). Experimental error in terms of the standard deviation and percentage average deviation was determined for each set of three experiments. From the results presented in Appendix B, it was found that the average deviation for all the determined parameters was < 2% for chars B and C; < 3% for char C2; and < 4% for char D2. Thus, experimental results from the TGA are reproducible. The distinct plots from the reproducibility tests for each of the chars are also included in Appendix B.

5.4 Effect of Operating Conditions on Char-CO_2 Gasification Reactivity

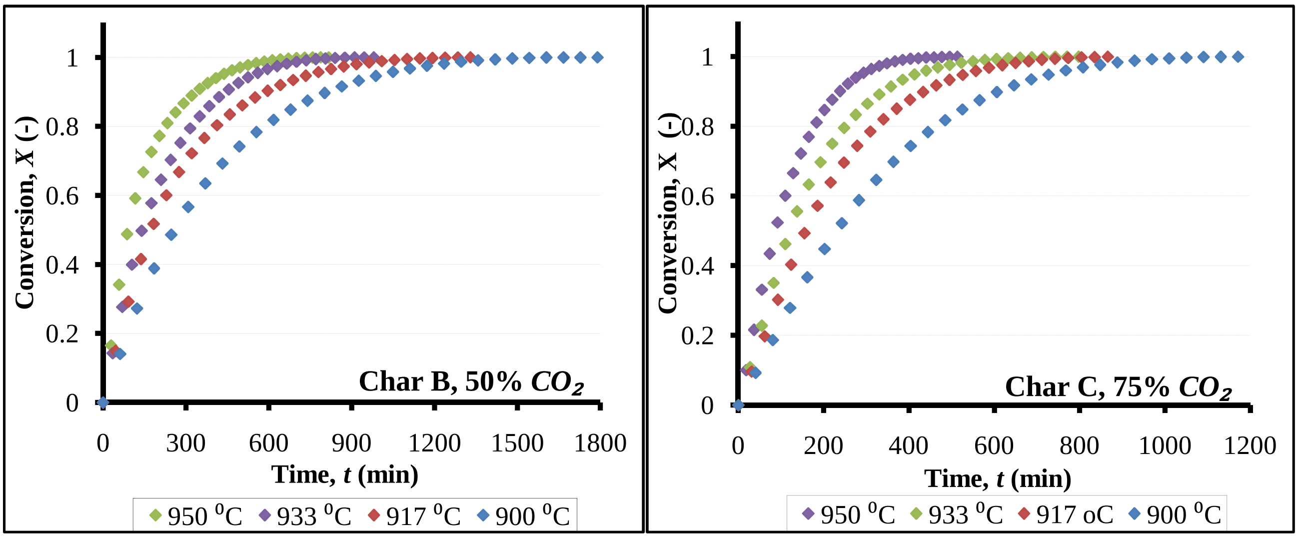
Apart from using four different char samples for the experiments, the isothermal temperature of reaction and CO_2 concentration were varied. The resultant effects of these variables are discussed in this section. It should however be noted that only a few of the results are shown here. More results are presented in Appendix B.

5.4.1 Effect of Isothermal Temperature of Reaction

The relative impact of the isothermal temperature of the char-CO_2 reaction (varied between 900 °C and 950 °C) is illustrated using the conversion-time plots in Figure 5.3. From the results, it is clear that that there is a relative increase in carbon conversion with increasing isothermal reaction temperature. This shows that the char-CO_2 gasification reaction follows Arrhenius type kinetics. These tendencies were observed in all the chars. Similar results were also obtained for different CO_2 concentrations in the reaction gas mixture.

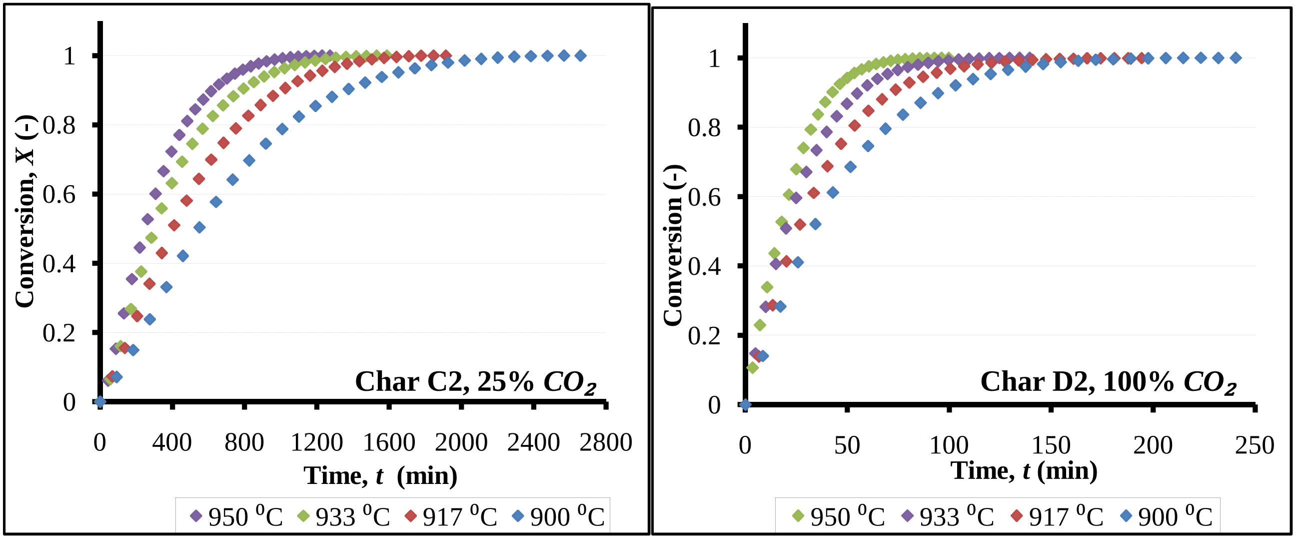
The same trend was observed by other investigators on char-CO_2 gasification reactions (Dutta *et al.*, 1977; Matsui *et al.*, 1987; Radovic *et al.*, 1985; Harris and

Smith, 1990; Miura *et al.*, 1990; Hampartsoumian *et al.*, 1993; Ochoa *et al.*, 2001; Fu and Wang, 2001; Sinağ *et al.*, 2003; Murillo *et al.*, 2006; Zhang *et al.*, 2006; Kajitani *et al.*, 2006; Zhang *et al.*, 2007; Kaitano, 2007; Everson *et al.*, 2006 and 2008a; Sangtong-Ngam and Narasingha, 2008; Wu *et al.*, 2008; Hattingh 2009).



(i) Effect of temperature on the CO_2 reactivity of char B at 50% CO_2, 0.875 *bar*

(ii) Effect of temperature on the CO_2 reactivity of char C at 75% CO_2, 0.875 *bar*



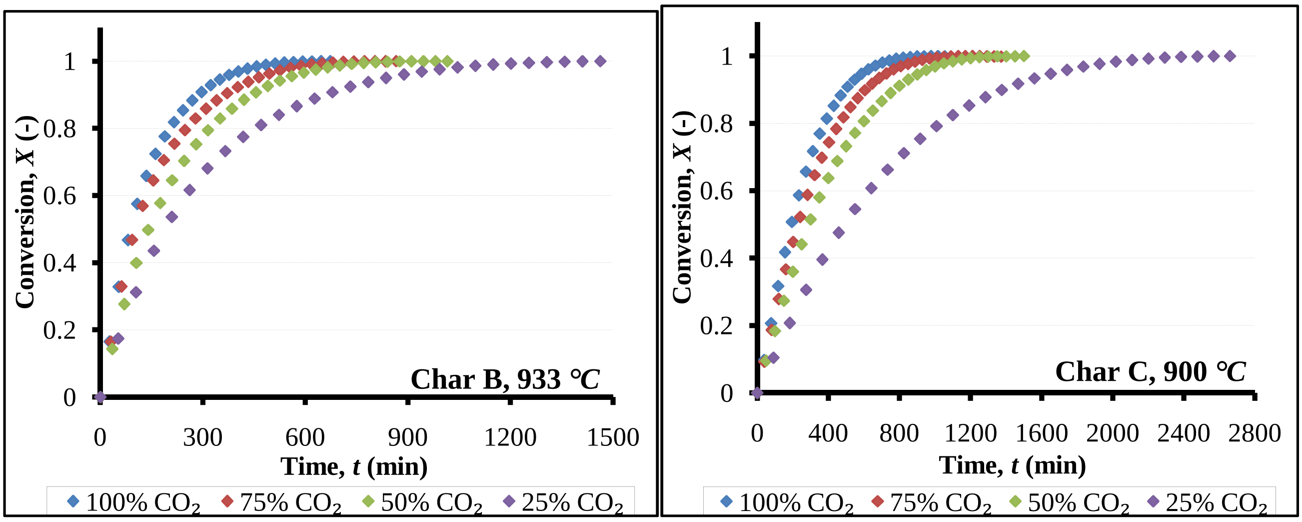
(iii) Effect of temperature on the CO_2 reactivity of char C2 at 25% CO_2 , 0.875 *bar*

(iv) Effect of temperature on the CO_2 reactivity of char D2 at 100% CO_2, 0.875 *bar*

Figure 5.3: Effect of temperature on the CO_2 reactivity of the chars at different constant CO_2 concentrations, 0.875 *bar*.

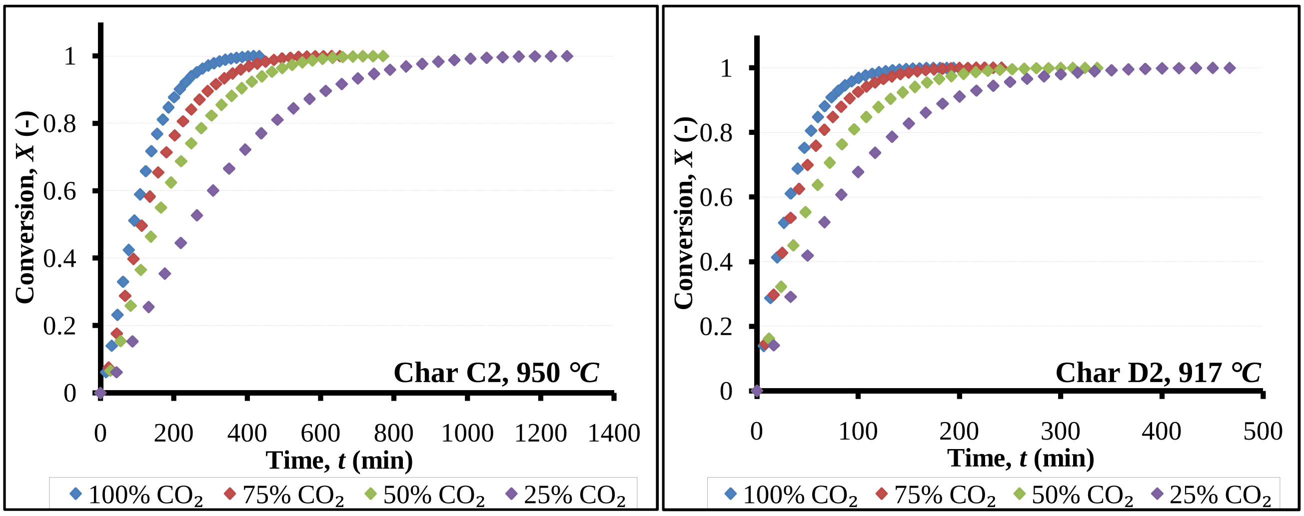
5.4.2 Effect of CO_2 Concentration in the Reaction Gas

Carbon dioxide gas composition was varied from 25 mole% to 100 mole%. The effect of changing concentrations of CO_2 in the reaction gas on the reactivity of the chars is given in Figure 5.4. It is evident from the results that increase in the concentration of CO_2 in the reaction gas mixture, culminates in a corresponding higher reactivity of the chars.



(i) Effect of CO_2 concentration on the reactivity of char B at 933 ℃, 0.875 *bar*

(ii) Effect of CO_2 concentration on the reactivity of char C at 900 ℃, 0.875 *bar*



(i) Effect of CO_2 concentration on the reactivity of char C2 at 950 ℃, 0.875 *bar*

(i) Effect of CO_2 concentration on the reactivity of char D2 at 917 ℃, 0.875 *bar*

Figure 5.4: Effect of CO_2 concentration on the char reactivity at various constant isothermal temperatures, 0.875 *bar*.

This can be explained by the fact that an increased CO_2 concentration means that more CO_2 molecules are available for the gasification reaction. The presence of larger amounts of CO_2 molecules in the reaction gas stream imply that more active sites in the char take part in the reaction resulting in a faster reaction rate. All the investigated chars exhibited similar trends, even at distinct isothermal reaction temperatures and correlate well with the results of other investigators (Harris and Smith, 1990; Zhang and Calo, 1996; Fu and Wang, 2001; Murillo *et al*., 2006; Zhang *et al*., 2006; Kaitano, 2007, Everson *et al*., 2006 and 2008a; Hattingh, 2009).

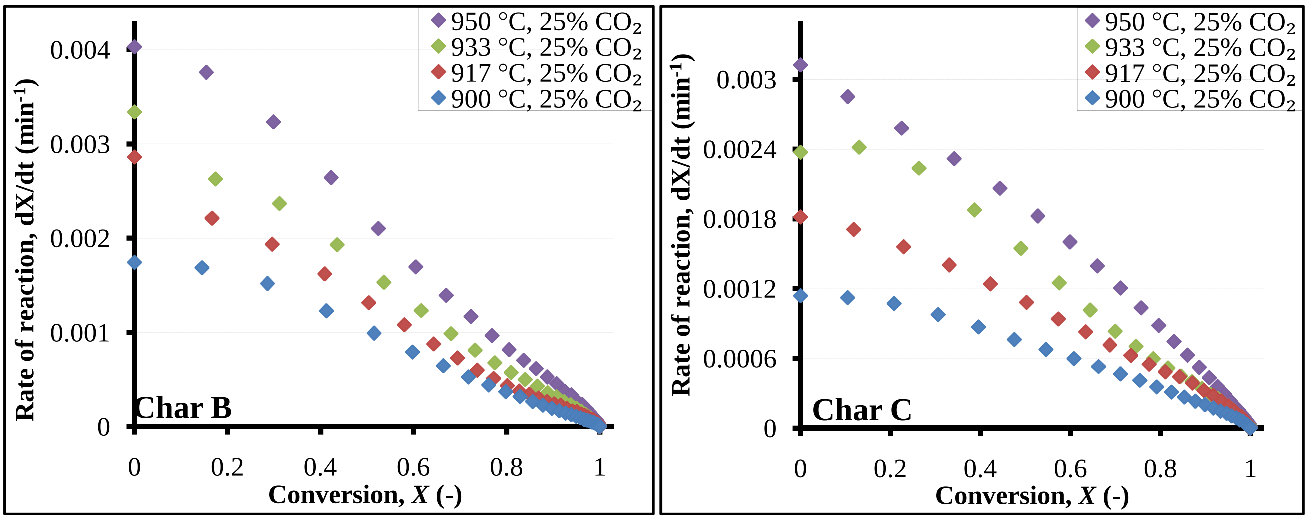
It was also observed that the reactivity at 25% CO_2 concentration was substantially lower than at the other concentrations. This may be attributed to the substantially lower amounts of CO_2 molecules in the reaction gas mixture, making it relatively difficult for the participation of all the char active site in the reaction. Kaitano (2007) also made a similar finding in char gasification experiments with CO_2 at lower concentrations of 20 mole% CO_2. More results are included in Appendix B.

5.5 Determination of the CO_2 Reactivity of the Chars

Reactivity of the chars in this study was confined to the initial reactivity, *R*, defined as (Jüngten, 1981; Czechowski and Kidawa, 1991; Senneca *et al*., 1998; Kajitani *et al*., 2006; Zhang *et al*., 2006; Kaitano, 2007; Everson *et al*., 2008a; Wu *et al*., 2008; Hattingh, 2009; Zhang *et al*., 2010):

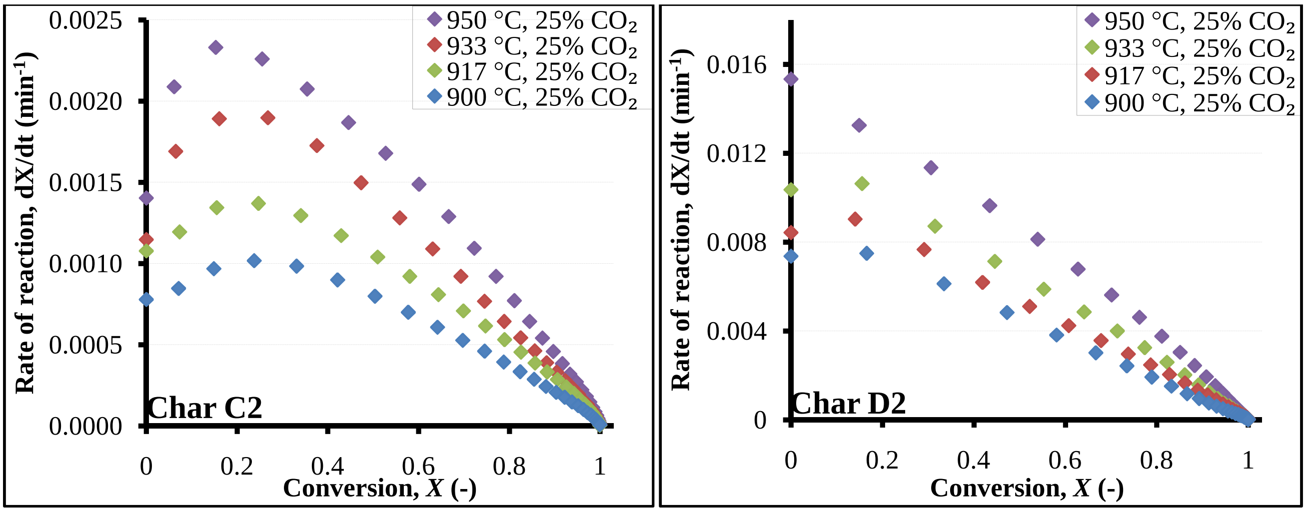
$$R = \left.\frac{dX}{dt}\right|_{t=0} \tag{5.2}$$

This was achieved by constructing a quantitative plot of the rate of reaction, dX/dt versus the carbon fractional conversion, *X*. It should be noted that the initial reactivity is also equivalent to the slope of the carbon conversion versus time plot at time, $t = 0$. The characteristic plots of dX/dt against X that was used to evaluate the initial reactivity of the chars at 25% *CO_2* concentration, 0.875 *bar* are given in Figure 5.5(i) - (iv); while similar plots at 50, 75 and 100% *CO_2* concentrations in the reaction gas mixture, are included in Appendix B. The summary of determined initial reactivity of all char samples is presented in Table 5.1.



(i) Rate of reaction versus conversion for char B at 25% CO_2, 0.875 *bar*.

(ii) Rate of reaction versus conversion for char C at 25% CO_2, 0.875 *bar*.



(iii) Rate of reaction versus conversion for char C2 at 25% CO_2, 0.875 *bar*.

(iv) Rate of reaction versus conversion for char D2 at 25% CO_2, 0.875 *bar*.

Figure 5.5: Rate of reaction versus fractional conversion for the chars at 25% *CO_2* concentration, 0.875 *bar*.

It is obvious from Figure 5.5 and Table 5.1 that char D2 had the highest initial reactivity, while char C2 exhibited the lowest reactivity of the four chars. It was also observed that for chars B, C, and D2, the maximum rate of reaction occurred at time, $t = X = 0$; while for char C2, the maximum rate of reaction occurred at time, $t > 0$ and $X > 0$. The reactivity of char D2 was found to be greater than the reactivity of the other chars by a factor > 4. Thus, the increasing order of the reactivity of the chars is: char C2 < char C < char B < char D2.

The initial reactivity of the chars were correlated with the various characteristic parent coals and subsequent chars properties to study their contribution and or influence to the char-CO_2 gasification reaction and kinetics.

Table 5.1: Determined initial gasification reactivity, *R* of the char at various operating conditions, 0.875 *bar*.

Temp. (*℃*)	y_{CO_2} (*mol. %*)	**Initial Reactivity, *R* ·10^{-3}** (*min^{-1}*)			
Char ID		**Char B**	**Char C**	**Char C2**	**Char D2**
900 *℃*	25%	1.56	1.02	0.92	6.87
917 *℃*		2.16	1.55	1.25	7.96
933 *℃*		2.51	2.21	1.67	9.57
950 *℃*		3.49	2.69	2.02	12.8
900 *℃*	50%	1.95	1.73	1.29	9.37
917 *℃*		2.86	2.01	1.78	12.0
933 *℃*		3.54	2.93	2.52	13.8
950 *℃*		5.53	4.43	3.37	19.0
900 *℃*	75%	2.24	2.18	1.72	12.3
917 *℃*		3.07	3.19	2.52	16.4
933 *℃*		4.92	4.15	3.06	20.5
950 *℃*		6.72	5.80	4.41	23.3
900 *℃*	100%	3.07	2.37	1.84	15.3
917 *℃*		3.93	3.96	3.09	19.7
933 *℃*		5.92	4.80	3.83	25.6
950 *℃*		8.07	6.50	5.52	27.2

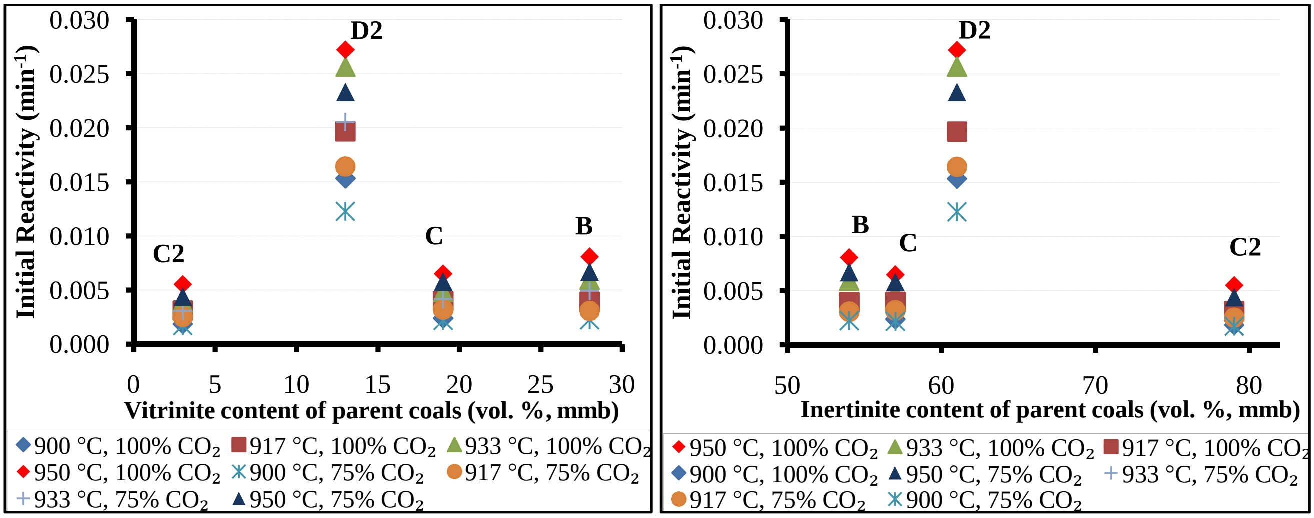
5.6 Effect of Coal and Char Properties on CO_2 Reactivity of the Chars

One of the objectives of this investigation is to correlate the chemical and physical properties of both coals and chars with the subsequent char reactivity towards CO_2 gasification. The influence of the parent coal's petrographic properties – such as total vitrinite content; total inertinite content; inertinite-vitrinite ratio; coal- *TRC* and *TIC; MI* and *RMI**; and rank parameter (vitrinite reflectance (*Rr%*)) – on the reactivity of the subsequent chars were assessed.

The effects of char properties such as petrographic properties (char- *TRC* and *TIC*) and chemical-structural or carbon crystallite properties (aromaticity, fraction of amorphous carbon, and degree of disorder index) were investigated. The catalytic influence of the high ash components of the chars were examined using the lumped parameter, the alkali index (*AI*). Physical structural properties such as D-R micropore surface area, H-K average micropore diameter, and porosity were also correlated with the reactivity results.

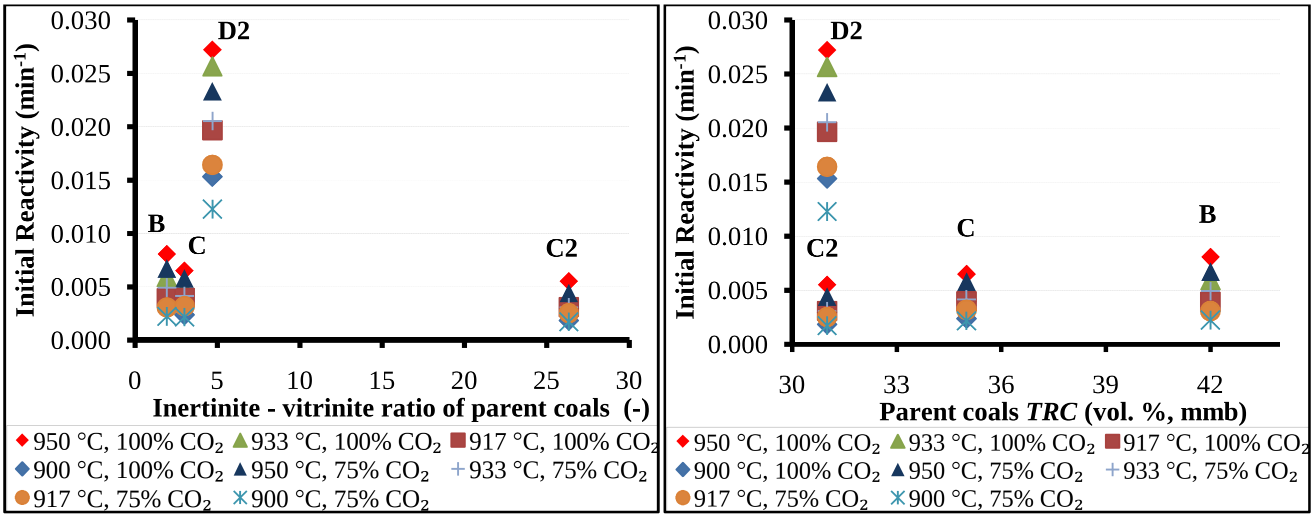
5.6.1 Effect of Parent Coals Petrographic Properties

It is generally accepted that coal vitrinites are more reactive and possesses better burnout characteristics than the coal inertinite macerals (Tsai and Scaroni, 1987; du Cann, 2008). It has also been proven that some inertinite maceral components are indeed "reactive" (Cloke and Lester, 1994). These were assessed by qualitative plots of the initial reactivity of the chars against the petrographic properties of the parent coals, including the inertinite-vitrinite ratios and coal *TRC* as shown in Figure 5.6(i)-(iv). Excluding char D2 that is entirely out of trend with respect to the petrographic properties of the parent coals, it can be deduced from Figures 5.6 (although the trend is rather insignificant) that the char reactivity for chars B, C, and C2, increases slightly with increasing volumes of coal vitrinites; and decreases with increasing proportions of inertinites in the parent coals.



(i) Initial reactivity of the chars versus vitrinite content of the parent coals

(ii) Initial reactivity of the chars versus inertinite content of the parent coals



(iii) Initial reactivity of the chars versus inertinite-vitrinite ratios of the parent coals

(iv) Initial reactivity of the chars versus the parent coals *TRC*

Figure 5.6: Relationship between the initial reactivity of the chars and the petrographic properties of the parent coals at 100% and 75% CO_2, 0.875 *bar*.

The reactivity of coal vitrinites is enhanced by their propensity to swell, expand and form vesicles that improve the porosity and increases the surface area of the reacting chars (Falcon and Snyman, 1986; Cloke and Lester, 1994; Tsai and Scaroni, 1987; du Cann, 2008). Although some inertinite components are reactive, most of the inertinite species observed in the four parent coals are the much denser components that do not easily "open up", soften or expand during devolatilisation. This results in denser chars with little or no significant augmentation of the char porosity or surface area (with the exception of char D2). This is responsible for the observed lower reactivity of the chars with increasing inertinite volumes in the parent coals (B, C and C2). It was also observed that the initial reactivity of the chars decrease with increasing inertinite-vitrinite ratios of the parent coals (though quite insignificant), with the exception of char D2 which again, was conspicuously off the trend. This is as expected, since vitrinites are far more reactive than inertinites (Jones *et al.*, 1985; Cai *et al.*, 1998; Megaritis *et al.*, 1999). Char C2 with the highest original coal inertinite-vitrinite ratio generally exhibited the lowest reactivity, while char B whose parent coal has the lowest inertinite-vitrinite ratio was more reactive in all the experiments.

The total reactive components (*TRC*) of the parent coals discussed earlier in Section 3.7.6, was also assessed for its influence on the initial reactivity of the chars. It was observed from Figures 5.5(iv) that initial reactivity increases with increasing volume of coal *TRC* for chars B, C and C2, although the exhibited trend is rather infinitesimal to be considered significant. The *TRC* of the precursor coals comprises of the reactive macerals: liptinites, vitrinites, reactive semifusinite and reactive inertodetrinite and its relative abundance in coal should be a valuable indicator of the expected reactivity of the chars. It was however observed that char D2 was again out of trend in this regard. The plot of the initial reactivity of the chars against the *TIC* of both the parent coals and the chars yielded a considerable scatter without any observed trend and was therefore not reported.

5.6.1.1 Effect of Maceral Index and Modified Reactive Maceral Index of the Parent Coals

Due to the inconsequential and unsystematic trends observed in the correlations of the parent coal’s petrographic properties to the subsequent chars reactivity, a further step was taken to confirm the observed negligible trends. It was thus considered that the use of a lumped predictive parameter that encompasses the combined effects of the maceral components would be useful. The maceral index (*MI*), proposed by Su *et al*. (2001) and the modified reactive maceral index (*RMI**) (Phiri, 2010), modified from the original reactive maceral index (*RMI*) proposed by Helle *et al*. (2003) was evaluated and assessed. The maceral index (*MI*) was evaluated from the expression (Su *et al*., 2001):

$$MI = \frac{TL + \left(TV / Rr^2\right)}{TI^{1.25}} \left(\frac{GCV}{30}\right)^{2.5} \tag{5.3}$$

Helle *et al.* (2003) modified the *MI* to *RMI* by considering the total inertinite denominator (*TI*) of Equation 5.3 to consist only of the inert components of the inertinites adjusted by the subtraction of reactive- semifusinite and inertodetrinite from the *TI* term. Thus, the *TI* was modified to the coal *TIC* (Table 3.22, Section 3.7.6), consisting of only the "inert" inertinite maceral components: inert semifusinite, fusinite/secritinite, micrinite and inert inertodetrinite. The *GCV* term was also removed and the *RMI* takes the form (Helle *et al*., 2003):

$$RMI = \frac{TL + \left(TV / Rr^2\right)}{TIC_{coal}^{1.25}} \tag{5.4}$$

Phiri (2010) went further by modifying Equation 5.4 to reflect the reactivity of the reactive semifusinite and reactive inertodetrinite not included in Equation 5.4 by Helle *et al*. (2003). By introducing TIC_{coal}, from Equation 3.16, Section 3.7.6, the proposed modified reactive maceral index (*RMI**) can be given as:

$$RMI* = \frac{TL + \left((TV + RSF + RINT) / Rr^2\right)}{TIC_{coal}^{1.25}} \tag{5.5}$$

Substituting Equation 3.12 (Section 3.7.6) into Equation 5.5, it can then, be re-written in terms of the coal- *TRC* and *TIC* as follows:

$$RMI* = \frac{TL + \left((TRC_{coal} - TL) / Rr^2\right)}{TIC_{coal}^{1.25}} \tag{5.6}$$

The *MI* and *RMI** were evaluated using Equation 5.3 and 5.6 respectively. All maceral components including the coal's *TRC* and *TIC* were normalised to mineral matter free basis (*mmfb*) as presented in Table 5.2.

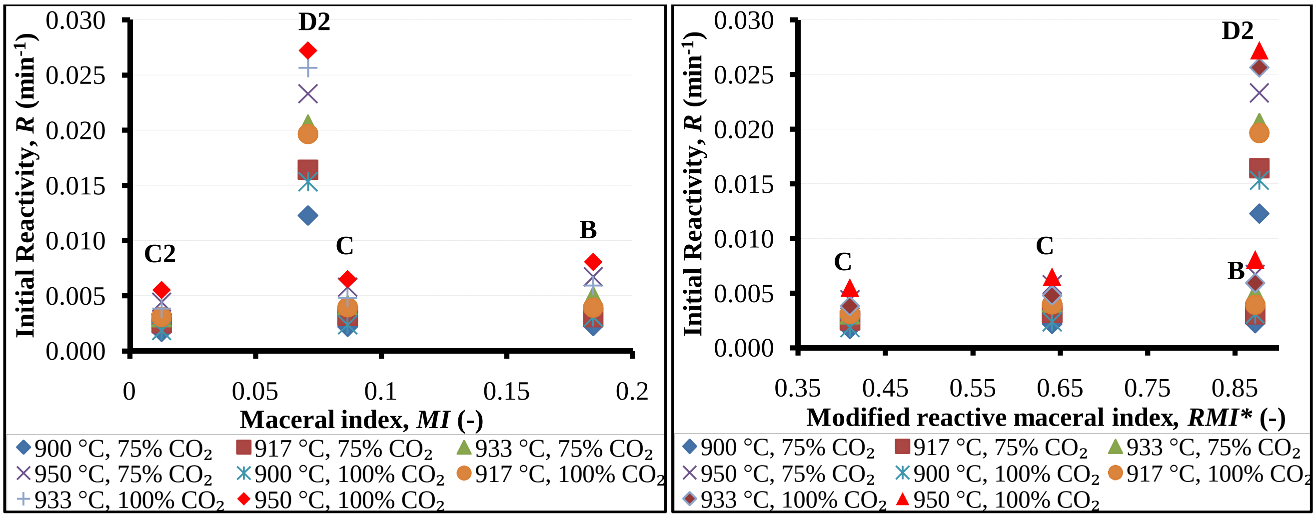
Table 5.2: Results used to evaluate the maceral index (*MI*) and the modified reactive maceral index (*RMI**) of the parent coals on mineral matter free basis (*mmfb*).

Sample ID	**Coal B**	**Coal C**	**Coal C2**	**Coal D2**
Total Vitrinite (*vol. %, mmfb*)	32.94	24.05	3.529	16.67
Total Liptinite (*vol. %, mmfb*)	3.529	3.797	3.529	5.128
Total Inertinite (*vol. %, mmfb*)	63.53	72.15	92.94	78.21
TRC_{coal} (*vol. %, mmfb*)	51.76	48.10	40.00	44.87
TIC_{coal} (*vol. %, mmfb*)	48.24	51.90	60.00	55.13
GCV ($MJ\cdot kg^{-1}$)	21.40	20.00	20.20	18.10
Vitrinite Reflectance, *Rr* (*%*)	0.670	0.720	0.750	0.560
MI (-)	**0.184**	**0.087**	**0.013**	**0.071**
RMI* (-)	**0.873**	**0.641**	**0.409**	**0.878**

The determined *MI* of the coals varied significantly from the reported results of Su *et al*. (2001), but correlated well with the findings of Hattingh (2009). This can be attributed to the fact that Su *et al*. (2001), investigated vitrinite-rich coals, while inertinite-rich Highveld coals were used both in this study and that of Hattingh (2009). The *RMI** results were found to be similar to the published results of Phiri (2010), in his investigation of inertinite-rich South African low grade coals.

The lumped parameters, *MI* and *RMI**, of the parent coals were correlated with the initial reactivity of the subsequent chars as given in Figure 5.7. Analogous to the petrographic properties of the coals a trend of infinitesimally increasing reactivity with increase in both indices was observed, this is however too insignificant to be considered as systematic or meaningful. Char D2 was again out of trend, while chars B, C, and C2 were more consistent.

These findings indicate that, although petrographic properties of parent coals do affect the quality and quantity of chars produced during pyrolysis, their influence on the char-CO_2 gasification reaction is quite limited.



(i) Initial reactivity of chars versus *MI* of the parent coals

(ii) Initial reactivity of the chars versus *RMI** of the parent coals

Figure 5.7: Relationship between initial reactivity of the chars and the *MI* and *RMI** of the parent coals at 100% and 75% CO_2, 0.875 *bar*.

5.6.1.2 Effect of Rank Parameter of the Parent Coals

Vitrinite reflectance of coal is a valuable tool in the determination of age or extent of maturation of coal in the coalification process, usually referred to as rank.

The relationship between the mean vitrinite random reflectance (*Rr%*) of the original coals and the reactivity of the chars is presented in Figure 5.8. A more meaningful and very systematic trend was observed. Char reactivity was found to decrease with increasing vitrinite reflectance *vis-à-vis* rank of the parent coal. Although coal B, C, and C2 were of the same rank (bituminous medium rank C), the slight variation in vitrinite reflectance was pronounced in the reactivity of the chars. Low reflecting inertinites have been found to be more reactive than higher reflecting inertinites (Cloke and Lester, 1994). Char D2 was derived from a lower ranked coal (bituminous medium rank D), and had the lowest vitrinite reflectance (*Rr%)* value of 0.56 %, and was generally the most reactive among the four chars.

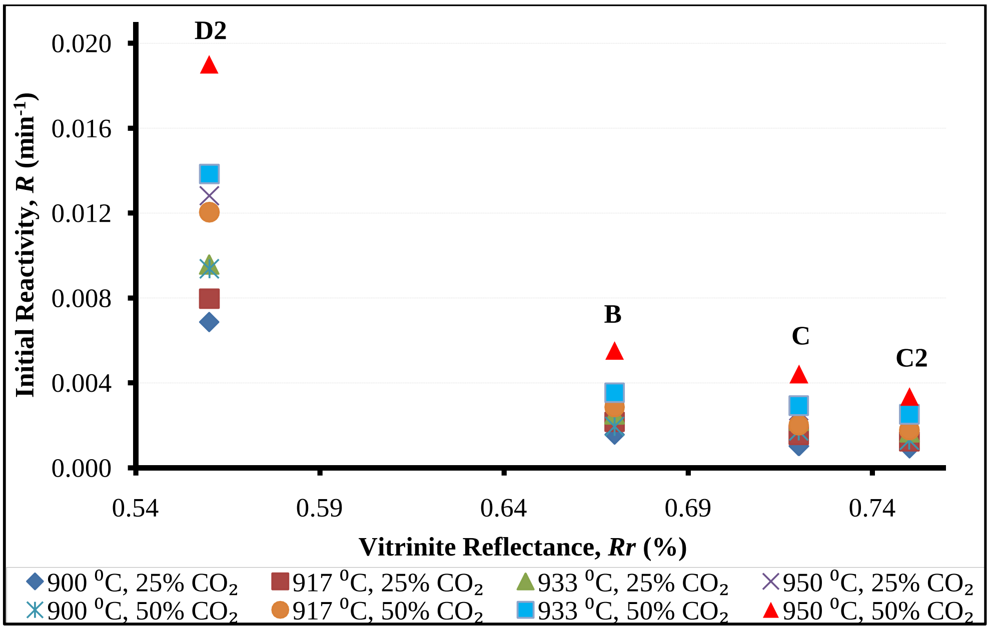


Figure 5.8: Relationship between the initial reactivity of the chars and the vitrinite reflectance (*Rr%*) of the parent coals at 100% and 75% CO_2, 0.875 *bar*.

However, the higher reactivity of lower ranked coals has long been known to be positively influenced by the inherent catalytic effects of ash components (Walker and Hippo, 1975; Laurendeau, 1978; Miura *et al*., 1989; Huang *et al*., 1991; Czechowski and Kidawa, 1991; Kyotani *et al*., 1993, Ye *et al*., 1998; Samaras *et al*., 1996; Hűttinger and Nattermann, 1994; Tomita, 2001; Kabe *et al*., 2004; Lee, 2007). This holds true for char D2 as it has the highest amount of ash (36.8 *wt. %*, *db*) compared to the other three chars.

5.6.2 Influence of Char Properties on Char-CO_2 Reactivity

5.6.2.1 Influence of Char Petrography (Char- *TRC* and *TIC*)

The development of char carbon forms with frequent tiny gas pores from coal vitrinites (Category A1 (i)), with fine walled more open network from coal reactives (Category A2) and thick walled isotropic coke from coal vitrinites (Category B7) in the transition to char process, improved some properties of the char (du Cann, 2007; Kaitano, 2007; Everson *et al*., 2008b). Notable among these enhanced properties are the surface area and porosity which play a vital role in the gasification reaction. It is therefore expected that an increase in the volume of total reactive components will correspondingly give rise to increased char reactivity. This was however, not fully validated by the insignificant and unsystematic trend observed in the qualitative plot of the char reactivity against the char *TRC* (char carbon forms) presented in Figure 5.9. From the result, a relatively infinitesimal increase in char reactivity was seen with increasing volumes of char *TRC* for chars B, C, and C2; while char D2 did fit into the trend.

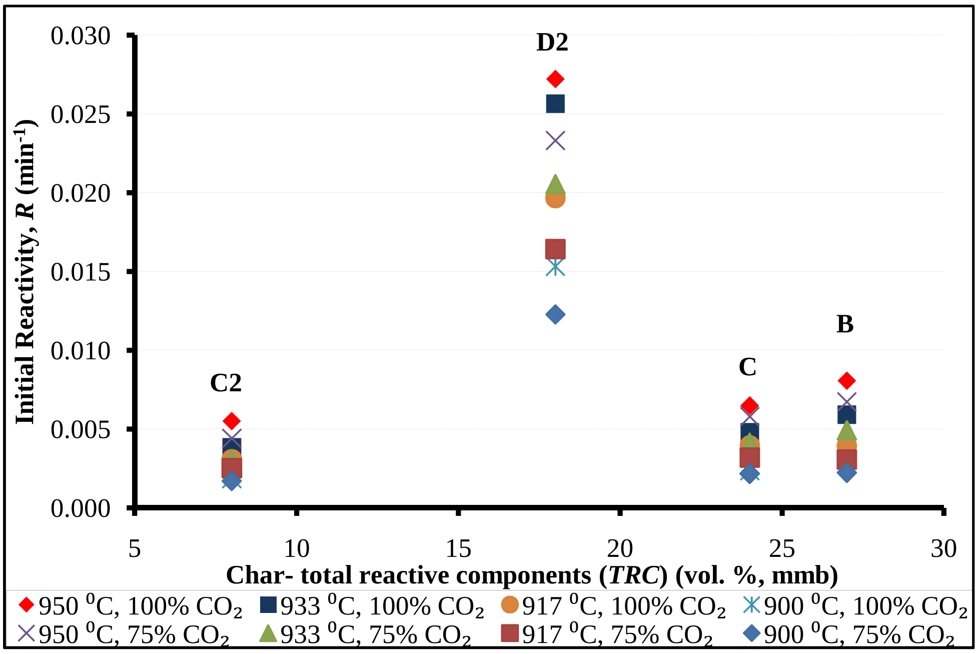


Figure 5.9: Relationship between the initial reactivity of the chars with the char *TRC* at 100% and 75% CO_2, 0.875 *bar*.

Like the parent coal's *TIC*, the qualitative correlation of the char's *TIC* with the initial reactivity of the chars, resulted in a dispersed scatter without any observed relationship and was therefore not reported. This further strengthens the fact that, petrographic properties do not effectively predict the char-CO_2 gasification behaviour of the chars in this investigation

5.6.2.2 Influence of Char Carbon Crystallite (Chemical Structural) Properties

5.6.2.2.1 Influence of Char Aromaticity

Aromaticity of carbonaceous materials refers to the ratio of aromatic carbons to the total aromatic and aliphatic carbons contained in them (Schoening, 1983; Lu *et al*., 2001, 2002a and 2002b; Maity and Mukherjee, 2006; Van Niekerk, 2008). It is the fraction of aromatic carbon atoms within the char crystalline structure (Lu *et al*., 2002b) and can describe the level of structural ordering of the carbons.

A plot of aromaticity of the chars versus the initial reactivity at 50% and 25% CO_2 concentrations is shown on Figure 5.10. It can be deduced from the result, that initial reactivity decreases with increasing aromaticity of the chars. Char D2 with the lowest aromaticity of 0.75 exhibited the highest initial reactivity, while char C2 with the highest aromaticity of 0.95 showed the lowest reactivity. Lu *et al*. (2002a and 2002b) reported increasing aromaticity with increasing fractional burnout which is an evidence that reactivity is reduced with increasing aromaticity of the chars as expected.

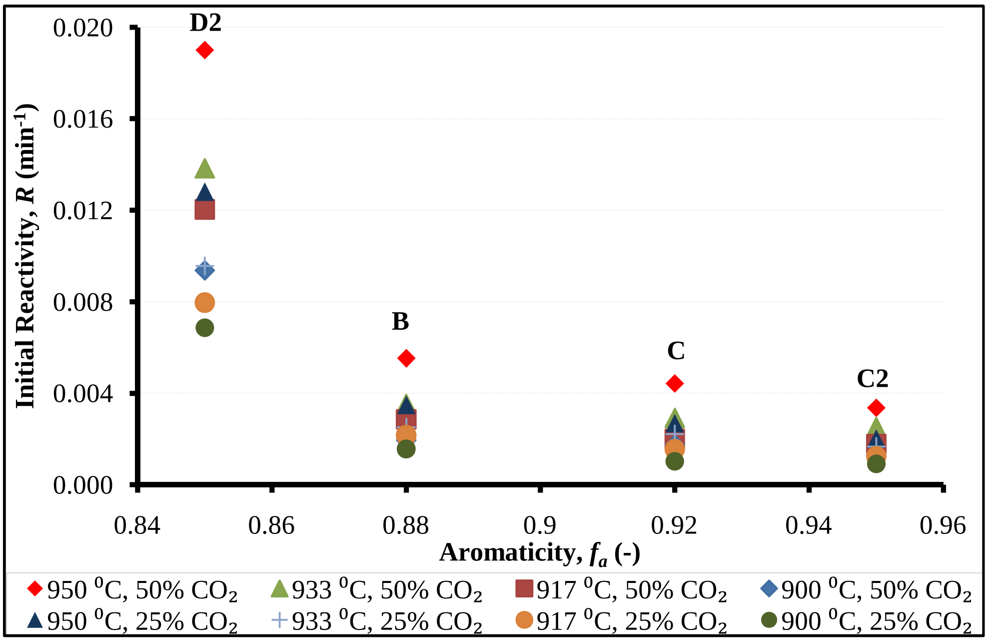


Figure 5.10: Relationship between the initial reactivity of the chars and the aromaticity of the char samples at 50% and 25% CO_2, 0.875 *bar*.

5.6.2.2.2 Influence of Fraction of Amorphous Carbon in Char

The influence of the amorphous carbon content of the chars on their initial CO_2 reactivity is illustrated in Figure 5.11. It is obvious from the plot, that the initial reactivity of the char increases almost linearly with increasing content of amorphous carbon. Amorphous carbon is the fraction of disordered, dis-orientated, non aromatic carbon contained in these chars (Franklin, 1950; Hirsch, 1954; Ergun, 1968; Lu *et al*., 2001, 2002a and 2002b; Kawakami *et al*., 2006; Wu *et al*., 2008).

This can be explained by the fact that increasing amorphous fraction of carbon indicates that the chars are less structurally ordered and may still contain some aliphatic and or pseudo-aliphatic carbons which are definitely more reactive than the aromatic carbons. It is also directly related to the aromaticity of the samples, as samples with higher aromaticity exhibited lower fractions of amorphous carbon as shown earlier in Figure 3.8(i) in Section 3.7.4.2. Lu *et al*. (2002a) and more recently, Wu *et al*. (2008) reported similar findings.

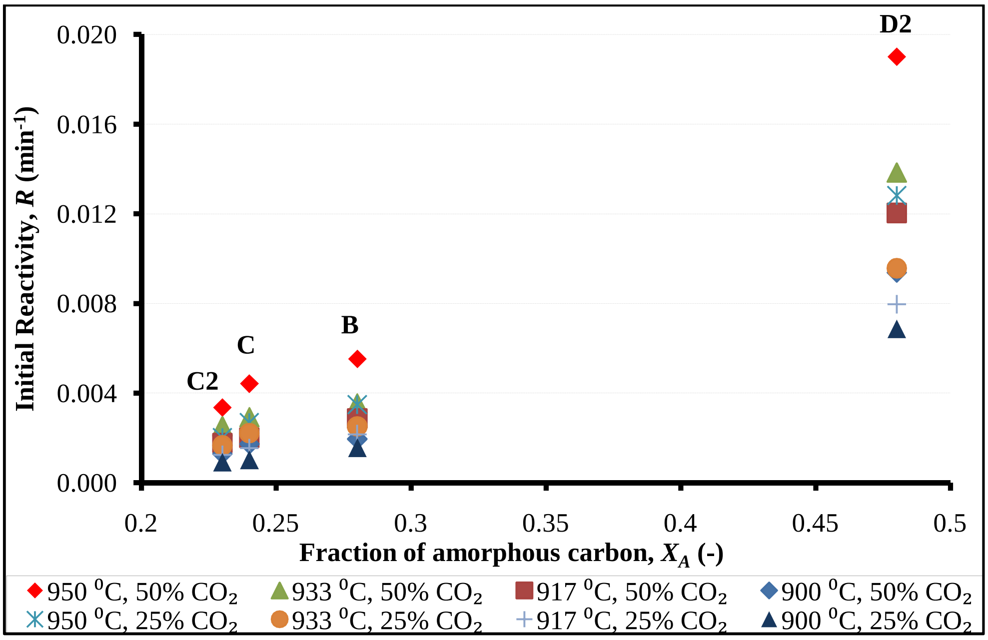


Figure 5.11: Relationship between the initial reactivity of the chars and the fraction of amorphous carbon in chars at 50% and 25% CO_2, 0.875 *bar*.

5.6.2.2.3 Influence of Degree of Disorder Index of chars

The fraction of amorphous carbon and aromaticity has been identified as having major influences on char reactivity. To correlate their lumped contribution to reactivity, Lu and co-workers (2002a) introduced the degree of disorder index (*DOI*) to quantify the disordered carbon in char. They found that reactivity increases with increasing *DOI*.

This observed trend is not unexpected as the *DOI* quantitatively refers to the carbon in amorphous phase and at the aliphatic side chains. An increasing *DOI* should therefore suggest an increasing fraction of amorphous carbon and decreasing aromaticity both of which will result to increased char reactivity. The impact of this index on the initial CO_2 reactivity of the four chars at 50% and 25% CO_2 in reaction gas mixture is presented in Figure 5.12. It is evident from the plot that reactivity increases linearly with increasing *DOI*. Char C2 with the lowest *DOI* is slowest, while Char D2 with the highest *DOI* has the highest reactivity.

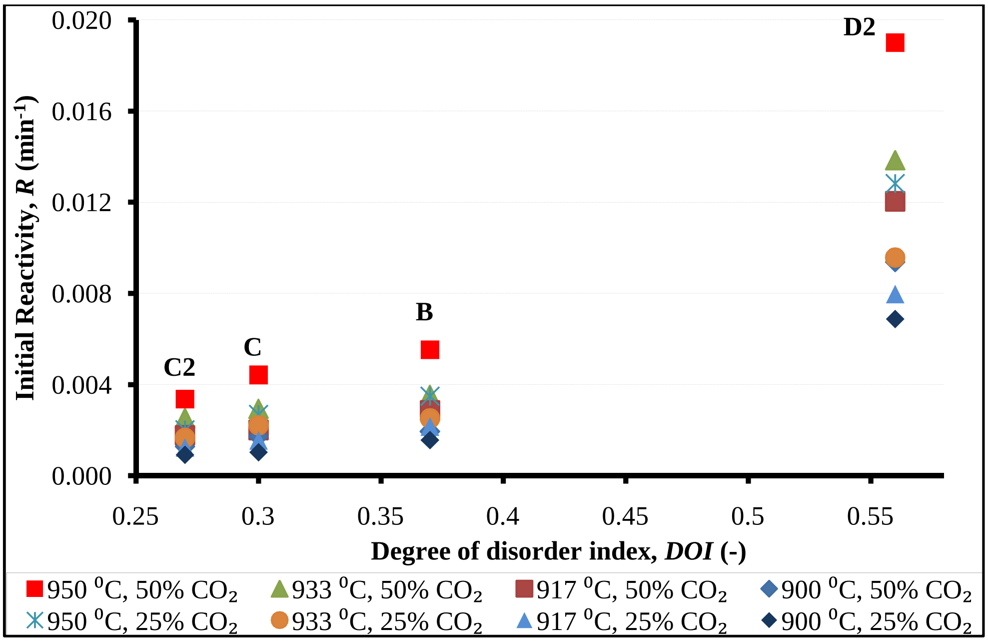


Figure 5.12: Relationship between the initial reactivity of chars and the degree of disorder index, *DOI*, at 50% and 25% CO_2, 0.875 *bar*.

5.6.2.3 Inherent Catalytic Effects of Ash Components of Chars

Char D2 has been characterised with some out-of-trend behaviour in most of the correlations with the petrographic properties of both coals and chars. To have a better understanding of this, the catalytic activity of the ash components was studied. A lumped parameter, the alkali index (Sakawa *et al.*, 1982; Zhang *et al.*, 2006) was evaluated from the XRF results. Alkali index, *AI*, is a parameter frequently used to describe the overall influence of catalytically active components in the ash of the reacting chars. The alkali indices of the chars were plotted against the initial reactivity at 50% and 25% CO_2 gas compositions. The result is given in Figure 5.13.

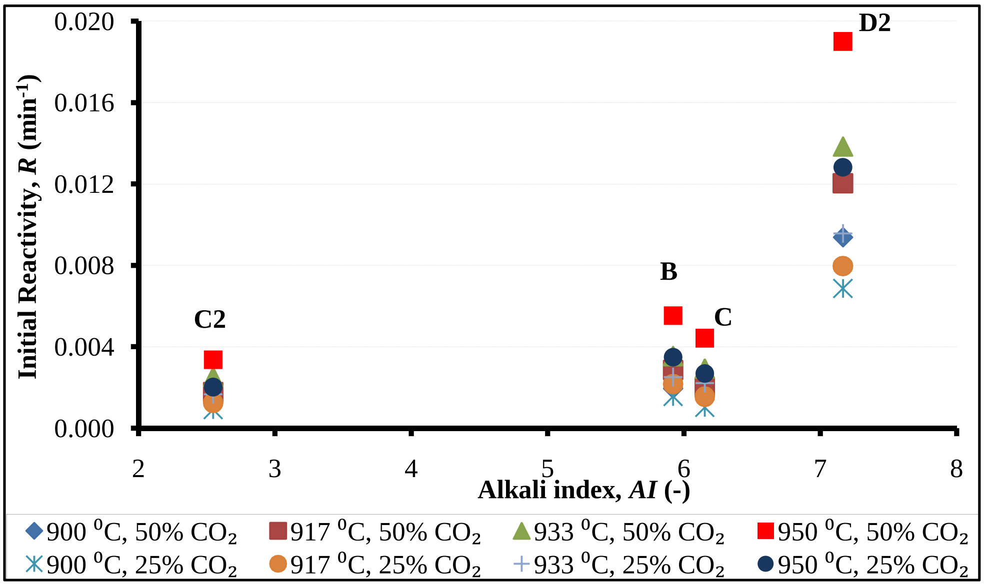


Figure 5.13: Influence of the alkali index on the initial reactivity of the chars at 50% and 25% CO_2, 0.875 *bar*.

It can be observed from these results that reactivity increases with increasing alkali index of the chars. Thus, the higher catalytic effect impacted on char D2 by its higher ash content and a corresponding higher alkali index coupled with the parent coals' lower rank may well be responsible for its higher initial reactivity despite its parent coal's low vitrinite content and higher inertinite-vitrinite ratio. These may be attributed to the combined catalytic effects of Ca^{2+}, Mg^{2+}, Na^{+}, Fe^{3+}, and K^{+} species in the char. Walker and Hippo (1975); Sakawa *et al.* (1982); Miura *et al.* (1989); Tomita (2001); Sun *et al.* (2004); Zhang *et al.* (2006); Lee (2007); and Zhang *et al.* (2010) reported similar findings.

5.6.2.4 Effect of Physical Structural Properties of Chars

5.6.2.4.1 Effect of Micropore Surface Area of Chars

The D-R micropore surface area was correlated with the initial CO_2 reactivity of the chars. It was observed that the initial reactivity of the chars increased almost linearly with increasing D-R micropore surface area as shown on Figure 5.14.

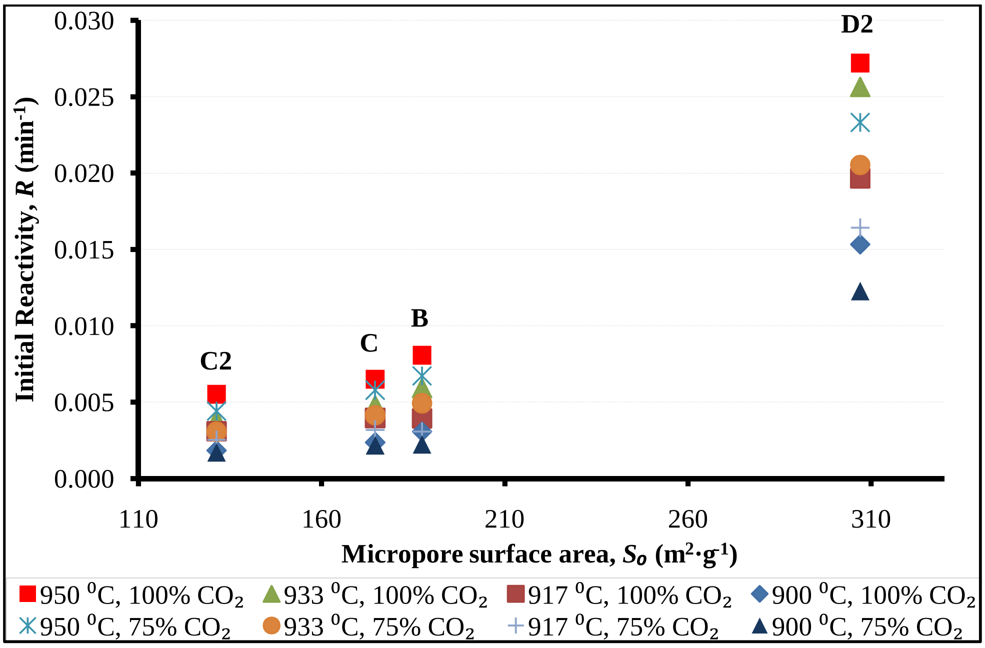


Figure 5.14: Influence of the D-R micropore surface area of chars on their initial reactivity at 100% and 75% CO_2, 0.875 *bar*.

This corroborates the result of other investigators that higher surface area promotes char reactivity (Ng *et al.*, 1988; Liu *et al.*, 2000; Kajitani *et al.*, 2006; Çakal *et al.*, 2007). The higher reactivity of Char D2 relative to the other chars was thus promoted, at least partially, by its higher micropore surface area, although some contributions may be expected from its mesopore surface area as the latter act as feeder pores (transitional pores) to the micropores (Ng *et al.*, 1988; Liu *et al.*, 2000).

However, due to the large differences usually observed between the micropore surface area and total pore area (meso- and macropore surface area), Dutta *et al.* (1977) as well as Kajitani *et al.* (2006) have proposed that the total reactive surface area can effectively be estimated by the micropore surface area.

5.6.2.4.2 Influence of Average Micropore Diameter of Chars

The micropore surfaces of chars have been reported as the preferred reaction surface area for gasification reactions (Ng *et al*., 1988; Çakal *et al*., 2007; Liu *et al*., 2000; Kajitani *et al*., 2006). Hence, the average micropore diameter should be able to give a qualitative description of the microporosity of the chars. Interestingly, char D2, with the lowest average micropore diameter (3.613 Å), has the highest initial reactivity. Char C2 with a higher average micropore diameter exhibited lower reactivity under the same reaction conditions. The result of this correlation is given in Figure 5.15.

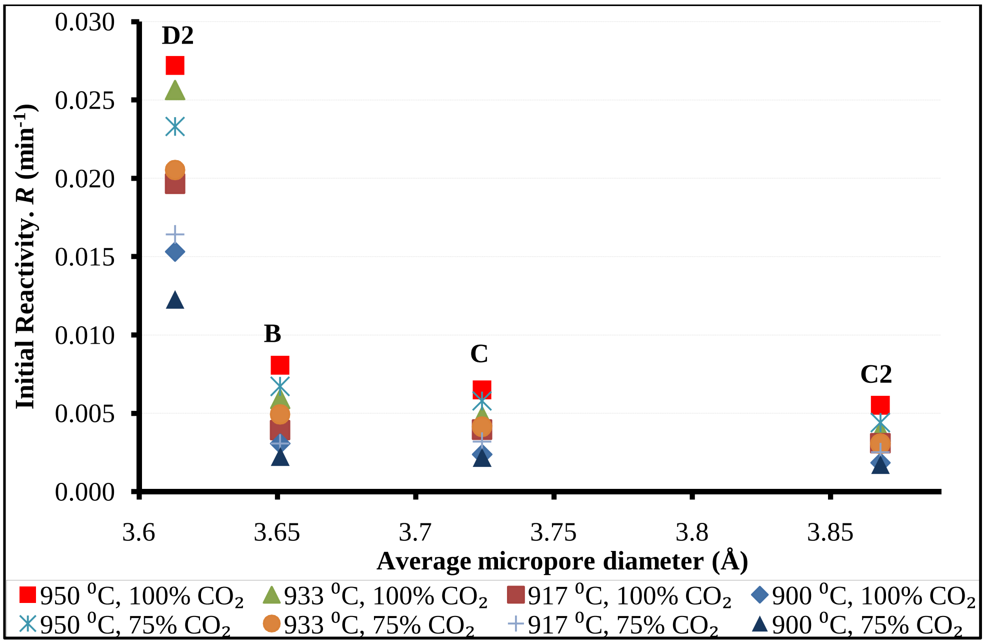


Figure 5.15: Influence of the average micropore diameter of chars on the initial reactivity at 100% and 75% CO_2, 0.875 *bar*.

5.6.2.4.3 Influence of Char Porosity

Char porosity is one of the char properties that undergoes significant improvement during the charring process with respect to the parent coals. The removal of volatiles from coal and the formation of vesicles, vacuoles and pores in the char enhance this property (Tsai and Scaroni, 1987; Senneca *et al*., 1998; du Cann, 2008).

The relationship between the initial char porosity and reactivity is presented in Figure 5.16. It can be deduced from the plot that the initial reactivity increases with increasing char porosity. An increase in char porosity has been reported to impact positively on the gasification reactivity of chars (Laurendeau, 1978; Senneca *et al.*, 1998) and this correlates well with the findings of this investigation.

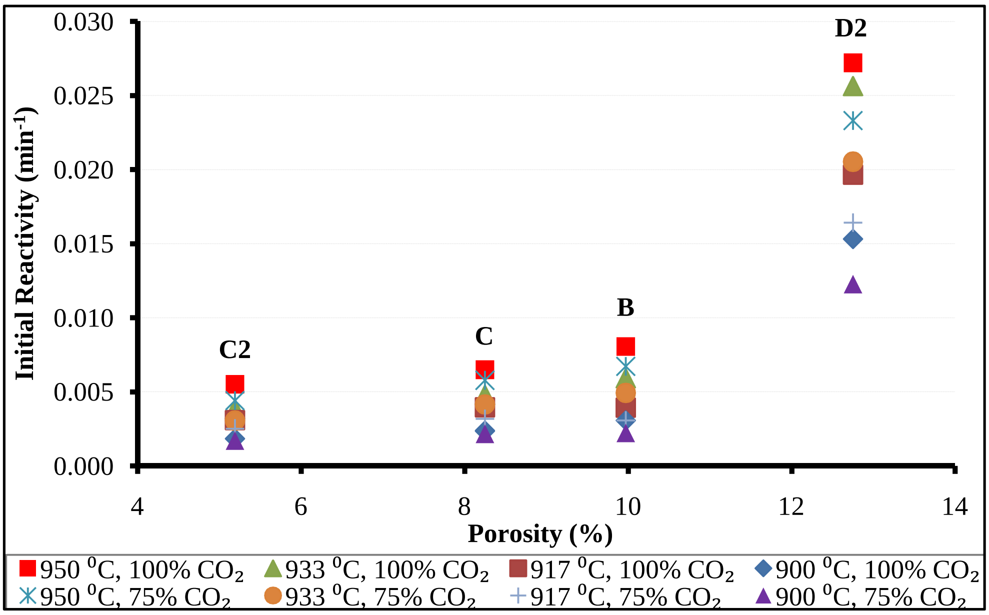
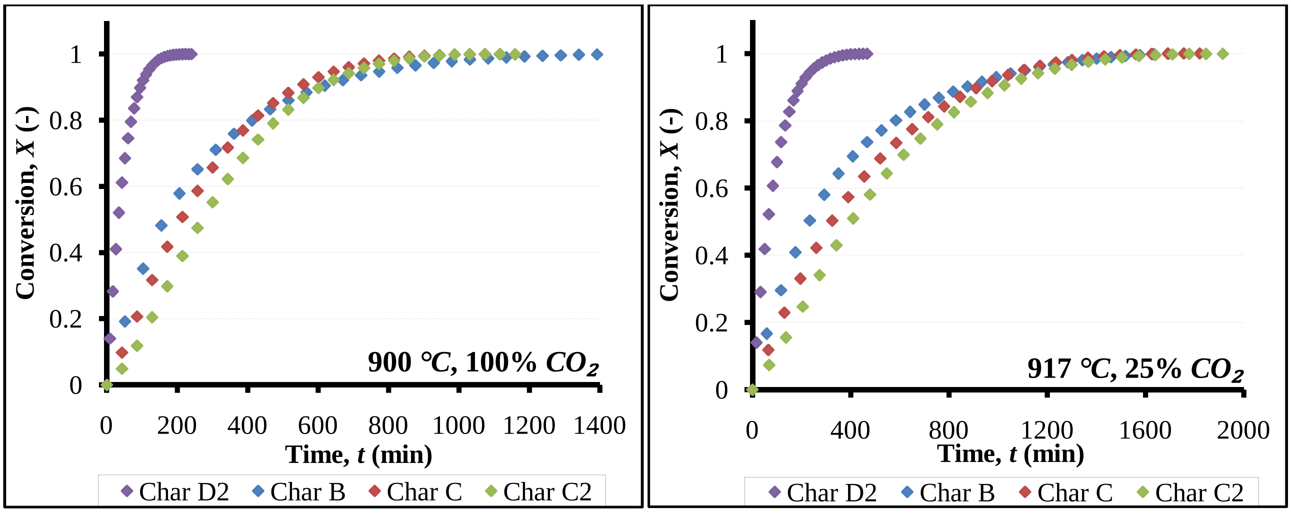


Figure 5.16: Influence of porosity of char on the initial reactivity at 100% and 75% CO_2, 0.875 *bar*.

5.7 Comparison of the CO_2 Reactivity of the four Chars

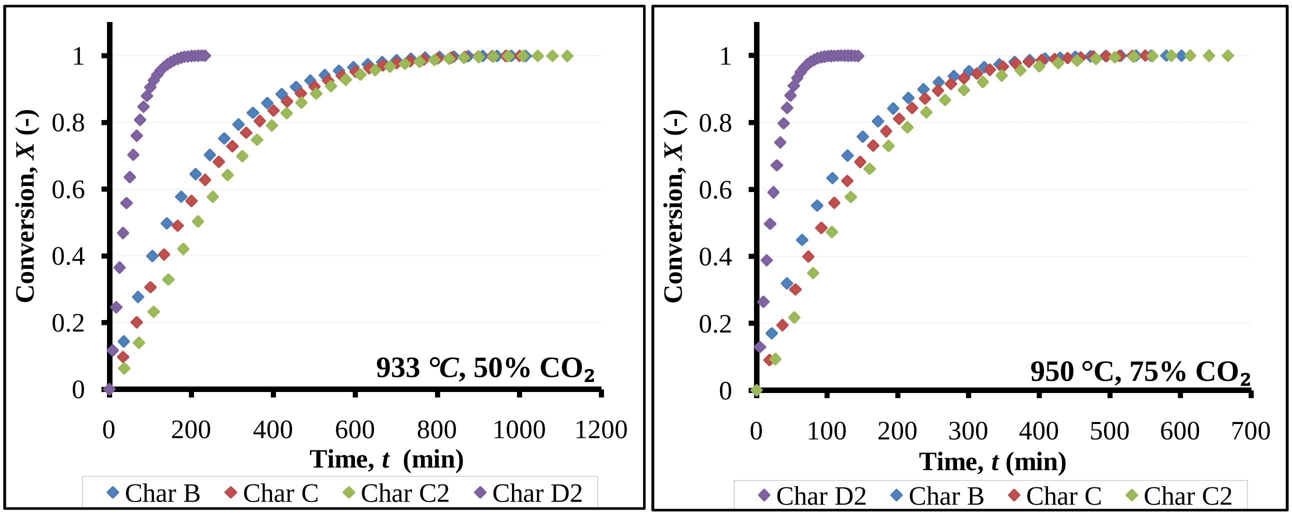
The reactivity of coal and chars has been used as benchmark for assessing their burn-out properties and performance during various conversion processes. The four chars used in this study were thus compared with each other at the same temperature and reaction gas composition. The results are partially presented in Figure 5.17 while the remainder are included in Appendix B. It is clear from the comparison plots that char D2 is more reactive than the other three chars: B, C and C2.

Char B generally exhibited a higher initial reactivity with respect to chars C and C2 until about 90%, followed by a very slow reactivity to completion. This has the effect that, although Char B has a higher initial reactivity when compared to chars C and C2, it also has a longer burnout time than for chars C and char C2. This may be attributed to the structural properties of char B and is an indication that its use in commercial systems may give rise to the presence of unburnt carbon in the ash or fly ash with reduced carbon efficiency (Cloke and Lester, 1994; Ouazzane *et al*., 2002; Helle *et al*., 2003; Styszko-Grochowiak *et al*., 2004)



(i) Comparison CO_2 reactivity of the chars at 900 °C, 100% CO_2, 0.875 *bar*

(i) Comparison CO_2 reactivity of the chars at 917 °C, 25% CO_2, 0.875 *bar*



(iii) Comparison CO_2 reactivity of the chars at 933 °C, 50% CO_2, 0.875 *bar*

(iv) Comparison CO_2 reactivity of the chars at 950 °C, 75% CO_2, 0.875 *bar*

Figure 5.17: Comparison of CO_2 reactivity of the chars at various temperatures and CO_2 concentrations, 0.875 *bar*.

Generally, reactivity of the chars increases in the order: C2 < C < B < D2. The very low reactivity of char C2 was possibly due to its possession of a very low fraction of amorphous carbon, low micropore surface area and the high aromaticity value (Sections 3.7.4 and 3.7.7; Tables 3.15 and 3.23). Char C2 was also found to contain more structurally ordered carbons than the rest of the chars, with a very low *DOI* (Davis *et al*., 1995; Senneca *et al*., 1998; Lu *et al*., 2002a; Kawakami *et al*., 2006; Wu *et al*., 2008). In addition, Char C2 also possessed the highest volumes of inert char carbon forms amongst the four chars (du Cann, 2008). Furthermore, char C2 had the lowest alkali index as well as lowest microporosity relative to the other chars (Sections 3.7.3 and 3.7.7; Tables 3.11 and 3.23).

Char D2 on the other hand exhibited very high micropore surface area; the highest proportion of amorphous carbon; the lowest aromaticity value; and a relatively higher alkali index, all of which indicate a higher level of disorderliness which impacts positively on reactivity (Sections 3.7.3, 3.7.4 and 3.7.7; Tables 3.15 and 3.23). The high *AI* value of char D2 should also mean that the inherent catalytic influence of the ash components may accelerate its gasification reaction (Laine *et al*., 1963; Kayembe and Pulsifer, 1976; Ng *et al*., 1988; Hüttinger and Natterman, 1994; Miura *et al*., 1989; Tomita, 2001; Zhang *et al*., 2006). Moreso, char D2 has the highest microporosity as well as the lowest average micropore diameter. Microporosity and micropore surface area have been identified as indicative of the preferred active surface area for CO_2 gasification reactions (Ng *et al*., 1988; Çakal *et al*., 2007; Liu *et al*., 2000; Kajitani *et al*., 2006).

Coal D2 is of lower rank (bituminous medium rank D) with respect to the other three coals (bituminous medium rank C) (Section 3.7.5; Table 3.16). It is generally accepted that chars derived from lower ranked coals are more reactive than chars derived from coals of higher rank (Laurendeau, 1978; Huang *et al*., 1991; Czechowski and Kidawa, 1991; Kyotani *et al*., 1993; Cloke and Lester, 1994; Samaras *et al*., 1996; Ye *et al*., 1998; Kabe *et al*., 2004; Lee *et al*., 2007). Thus, the higher reactivity of char D2 was influenced by the rank parameter.

However, Hüttinger and Natterman (1994); Miura *et al*. (1989); Tomita (2001) and Lee (2007) had attributed the higher reactivity of lower ranked coals partially to the catalytic activity of their ash components, which also applies to char D2.

5.8 Summary

With regard to the operational variables used in this study, the char-CO_2 gasification reactivity was found to follow the Arrhenius type kinetics. Reactivity of the chars was observed to increase with increasing temperature as well as CO_2 concentration in the reaction gas mixture.

A comparison between the reactivity of the four chars shows that char reactivity increases in the order: char C2 < char C < char B < char D2. The reactivity of char D2 was found to be higher than the reactivity of the three other chars by a factor > 4.

The high reactive nature of char D2, although lower in parent coal vitrinite content and higher in inertinite-vitrinite ratio in comparison to the chars B and C, can probably be attributed to its higher micropore surface area and microporosity (Ng *et al*., 1988; Liu *et al*., 2000; Çakal *et al*., 2007; Zhang *et al*., 2010), higher alkali index (Sakawa *et al*., 1982; Zhang *et al*., 2006) and higher fraction of amorphous carbon (Lu *et al*., 2002a; Wu *et al*., 2008). Its lower aromaticity also means that there are more disordered carbons in char D2 with respect to the other chars. The lumped parameter of structural disorderliness, the *DOI* was also found to have a positive effect on the reactivity of the chars and corroborates the results of char aromaticity and fraction of amorphous carbon in the chars.

Except for the rank parameter - the vitrinite reflectance, the parent coal's petrographic properties did not exhibit systematic or significant trends when correlated with the subsequent char reactivity. The only meaningful observation was that, char reactivity increases with decreasing vitrinite reflectance, which implies that reactivity decreases with increasing rank. Hence, char C2 which was generally marked with lowest reactivity had its parent coal possessing a higher vitrinite reflectance (0.75 *Rr*%), a very high inertinite content (79 *vol. %*, *mmb*) and high inertinite-vitrinite ratio of 26.3. Char D2 was however, derived from a lower ranked coal (0.56 *Rr%*).

An overview of the influence of the parent coal and subsequent char properties on the char-CO_2 gasification reactivity, show that major factors impacting on the reactivity of the four chars as it pertains to this study can be outlined as follows:

- Parent Coal properties:
  - ✓ Rank of parent coal (Vitrinite reflectance)
- Char properties:
  - ✓ Carbon crystallite (Chemical structural) properties:
    - Aromaticity
    - Fraction of amorphous carbon
    - Degree of disorder index
  - ✓ Catalytic effects of mineral matter (Alkali index)
  - ✓ Physical structural properties:
    - Micropore surface area
    - Average micropore diameter
    - Porosity