

# CHAPTER 7

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## **7.0 CONCLUSION AND RECOMMENDATIONS**

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### **7.1 Introduction**

The effects of the characteristic chemical and physical properties of both the parent coals and the subsequent chars on the char- $CO_2$  gasification reaction kinetics have been elucidated in this dissertation. In this chapter, a summary of the major findings and the conclusions reached during the investigation are presented. Prospects and relevant recommendations for future studies are also provided.

## 7.2 General Conclusions

The general conclusions derived from this investigation are as follows:

- Petrographically, the four parent coals were characterised as inertinite-rich and have high ash contents. The vitrinite reflectance are within a small range of 0.56 - 0.75  $R_r\%$  in all the coal samples. These coal samples are thus classified as bituminous medium rank C to D. Considerable shift to higher values were observed in the total maceral reflectance scans of the chars, relative to  $R_{sc}\%$  of the parent coals. The pure mono-maceral, inertite was observed to be the most abundant in all four coals. The transition from coal to char led to the formation of various char carbon forms in the chars. Greater volumes of dense and thicker walled char networks were formed from coal inertinites, while coal vitrinites yielded less dense chars with tiny gas pores and minor proportions of isotropic coke. Coal reactive macerals formed fine walled, more open char networks with a rather low abundance in all four chars. The total reactive components ( $TRC$ ) generally decreased from coals to the chars with losses  $>36.5\%$ . The total inert components ( $TIC$ ) exhibited gains in the transition from coals to chars, with gains of 12.2 to 24.4%, except char C2 with neither gain nor loss (0%). These losses and gains may be attributed to the conversion of some of the “reactive” macerals in the coals to inert char carbon forms during the pyrolysis reactions, while the 0% loss observed in char C2 may be due to its content of higher volume of partially reacted macerals.
- Except for the maceral contents and inertinite-vitrinite ratios, significant changes in chemical, physical and structural properties were not observed in the four original coals. The subsequent chars prepared at 900 °C with a holding time of 70 minutes, however, did exhibit differences, both amongst the chars and from the parent coals. Chemical properties such as fixed carbon, elemental carbon, and ash contents increased, while elemental oxygen and hydrogen content decreased from coal to the chars. Volatile matter and moisture contents were substantially reduced from the coals to the chars. There were however, some traces of both moisture and volatiles in the chars. These significant changes resulted in an increase in skeletal density, aromaticity and a corresponding reduction in the fraction of amorphous carbon and the degree of disorder index of the chars.

- On the physical and structural properties; both the micropore surface area and microporosity increased, while average micropore diameter decreased from coals to chars due to the evacuation of volatiles and the opening of hitherto “blind or inaccessible” fine pores. The increasing order of magnitude of the micropore surface area and microporosity of the original coals did, however, change in the chars. Carbon crystallite lattice parameters determined for the parent coals and the subsequent chars revealed that the chars are more structurally ordered, more compact and condensed (smaller in size) than the original coals (evident from the decreased lattice parameters:  $L_a$ ,  $L_c$  and  $N_{ave}$  and increased  $d_{002}$  from coals to chars). Although, these changes have been largely attributed to the heat treatment during char production, the mechanism of structural ordering is not well understood. The increasing order of magnitude for both the fraction of amorphous carbon and the structural disorderliness was found to change from coals (coals: B < C < C2 < D2) to the chars (chars: C2 < C < B < D2). XRD mineral analysis confirmed the predominance of clay and quartz mineral in both coal and char samples which was corroborated by the XRF ash component analysis of the chars. The alkali index, evaluated for the char samples, revealed that the reactivity of char D2 was enhanced by inherent catalysis of the inorganic components relative to the other chars.
- The gasification reactivity of the four char samples ( $1000 \mu\text{m} < d_p < 1120 \mu\text{m}$ ) was determined on a Thermo 500 TGA using various concentrations (25 - 100 mol. %) of  $\text{CO}_2$  in the  $\text{CO}_2\text{-N}_2$  reaction gas mixture in the temperature range of 900 - 950 °C. Reactivity of the chars was found to increase with increasing temperature as well as  $\text{CO}_2$  composition in the reaction gas mixture. The comparison of the reactivity of the four chars shows that, the reactivity of the chars generally 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 other three chars by a factor > 4.
- The correlation of the parent coal petrographic properties to the reactivity of the respective chars gave insignificant trends except for the rank parameter – the vitrinite reflectance. Lower reflecting inertinite (Char D2) was found to be more reactive than the other chars (chars B, C and C2). Char C2 with the highest vitrinite

reflectance was least reactive. The maceral index; the modified reactive maceral index; and the coal- and char- *TRC* and *TIC* all failed to give a systematic trend.

- The correlation of char properties with char gasification reactivity shows systematic and significant trends. The reactivity of the chars was found to increase with increasing fraction of amorphous carbon, degree of disorder index, and alkali index, and to decrease with increasing aromaticity of the chars. Thus, the extent of structural disorderliness is a good predictor of char reactivity. With regard to the influence of the physical properties of the chars, reactivity was observed to increase with increasing micropore surface area and porosity and to decrease with increasing average micropore diameter of the chars.
- The structural parameters,  $\psi$ , determined using the random pore model (RPM) for chars B, C, C2 and D2, are 1.11, 1.75, 2.58, and 1.57 respectively. The time scale parameter, the time factor,  $t_f$ , determined for each experiment was approximately the same as the initial reactivity evaluated from the experimental data. The RPM predicted reactivity,  $t_f$ , also confirmed the higher reactivity of char D2 relative to the reactivity of the other chars by a factor  $> 4$ . The activation energy obtained for the char- $CO_2$  gasification reactions was between  $163.3 \text{ kJ}\cdot\text{mol}^{-1}$  to  $235.7 \text{ kJ}\cdot\text{mol}^{-1}$ , while the order of reaction with respect to  $CO_2$  concentration ranged from 0.52 to 0.67. The lumped pre-exponential factor,  $k'_{so}$ , determined for the four chars, was  $5.22 \cdot 10^8$ ,  $4.36 \cdot 10^7$ ,  $1.12 \cdot 10^8$ , and  $2.69 \cdot 10^5 \text{ min}^{-1}\text{bar}^{-1}$  for chars B, C, C2, and D2 respectively. The gasification reaction with  $CO_2$  was found to be kinetically chemical reaction controlled for all four chars studied in this investigation within the specified operating conditions and all the experimental results were satisfactorily described by the RPM (Regime I). The RPM was validated by a parity plot of the experimental conversions against the model predicted conversions which followed a linear trend for the four chars. The fitting of the RPM conversions and conversion rate data to the experimental conversions and conversion rates also gave adequate fits.

### 7.3 Contributions to Knowledge Base of Coal Science and Technology

The following results derived from this study are considered important contributions to the knowledge base of coal science and technology:

- ❖ The detailed characterisation of the chemical and physical properties of both the parent coals and the subsequent chars has revealed that the properties of the chars are different from those of the coals. Detailed petrographic analysis has shown that there is a considerable reduction in the total reactive components (*TRC*), while the total inert components (*TIC*) increase from coal to char.
- ❖ Carbon crystallite analysis using XRD (which has not been previously studied for these four samples) was applied to study the carbon crystallite evolution from coals to chars from which the carbon aromaticity, fraction of amorphous carbon and the degree of disorder in the samples were evaluated. Results from this analysis show that the charring process changes the carbon crystallite such that the increasing order of structural ordering in the coals change when compared with the increasing order of structural ordering in the chars. Furthermore, the crystallite lattice was elucidated by the analysis result.
- ❖ The use of the characteristic lumped parameters such as the alkali index and the degree of disorder index to adequately predict the reactivity and the gasification behaviour of the chars is regarded as an important contribution to coal science and technology. Lumped parameters determined from the petrographic results of the coals (*MI* and *RMI\**) did not give meaningful correlations with the char reactivity results.
- ❖ The significant changes in chemical and physical properties of chars has had the effect that the correlation of char reactivity with the parent coal properties (including the lumped parameters- *MI* and *RMI\**) did not give meaningful or systematic trends. Thus, a better prediction of the reactivity of chars should be based on the char properties, because the subsequent chars are different from the parent coals. This is one of the major contributions of this study to the knowledge base of coal science and technology.

## 7.4 Recommendations for Future Studies

Based on the findings of this study, the following recommendations are proposed for further investigations:

- ❖ A detailed characterisation of the carbon crystallite of the coals and subsequent chars using  $^{13}\text{C}$  NMR and HRTEM. This will enable the study of other properties of the carbon BSU not covered by XRD as well as validate the results obtained from the XRD analysis.
- ❖ Investigation of chars produced from coals of different ranks and maceral concentrates should be undertaken with a focus on detailed characterisation (chemical and physical properties) of the parent coals and chars and on gasification reactivity tests. This will give a better understanding of changes in properties, including carbon crystallite evolution from coals to chars and broader correlations to the reactivity of the chars.
- ❖ The investigation of char gasification characteristics with mixtures of two or more of gasifying agents ( $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2$ , and *Air*) in order to study the combined effect of the gasifying agents and products as well as any inhibition and or promotion arising from the combination(s) during the gasification process. This will give a more pragmatic application to gasification studies and will yield results that can describe the practical gasification process better.
- ❖ The investigation of changes in properties imparted to chars prepared at different charring temperature (up to 1400 °C) and the subsequent reactivity of the chars. This will immensely help in a better understanding of changes in the carbon BSU. This will also imply that some reactivity experiments will have to be carried out at higher temperatures (> 1200 °C) which may shift the kinetic control to diffusion controlled (Regime II). A study of this type will be ideal as most practical gasification processes occur in this regime.
- ❖ Pilot plant studies of different combustion and gasification systems should also be undertaken. This will give a more realistic result that can easily be applied or retrofitted to practical gasification systems.