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**REACTIVITY CHARACTERISATION OF
AUSTRALIAN COALS FOR USE IN ADVANCED
TECHNOLOGIES**

RESEARCH REPORT 35

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1 Executive Summary

Previous work within the CRC for Black Coal Utilisation developed bench-scale techniques to generate volatile yield and intrinsic char reactivity data under conditions relevant to advanced coal utilisation technologies. This consisted of two stages: measurement of coal pyrolysis yields in a pressurised wire-mesh reactor (WMR), and measurement of the reactivity of chars produced in this wire-mesh reactor using a pressurised thermogravimetric analyser (PTGA).

This report presents the results of the application of these techniques to produce a comparative volatile yield and char reactivity database for the CRC coal suite. The bench-scale wire-mesh reactor was used to characterise the CRC coals' volatile yields under high heating rates and pressures, producing chars representative of those formed in high-pressure combustion and gasification processes. The pressurised thermogravimetric analyser was then used to measure the chemical reactivity of these chars to oxygen, carbon dioxide and steam, at reactant pressures relevant to modern gasification systems.

These data reinforce previous CRC research, which showed that—even with the enhancing effect of a high heating rate—increasing pyrolysis pressure decreases volatile yields. The extended data set obtained here revealed some rank-related effects on this trend, namely, higher ranked coals tend to show more of a reduction in volatile yield with increasing pressure than lower rank coals. In fact, the sub-bituminous coals investigated showed volatile yields at increased pressure higher than their proximate volatile matter content, although this yield is expected to decrease with further increases in pressure.

The reactivity data obtained using the chars produced in the WMR revealed marked differences between the three reactants. Measured reaction rates for chars reacting in CO₂ showed a rank-related effect, in that the chars made from higher-ranked coals had a slower measured reaction rate. Such an effect was less prominent for chars reacting in O₂ and H₂O. The surface areas of the chars contributed significantly to the CO₂ reaction rates; less so to the reaction rates of the chars with O₂ and H₂O. This reinforces the notion that whilst surface area is an important factor when considering the reactivity of a coal char, it is not the sole contributor, and under high-pressure conditions other factors such as carbon crystallinity and mineral matter catalysis can still be significant.

The data presented in this report are of the form that allow them to contribute to a comparative assessment of the coals for use in advanced technologies. The volatile yield data obtained are more representative than estimates based on a proximate volatile matter assay, the char samples produced are similar in terms of both physical structure and chemical reactivity to those found in combustion and gasification applications, and the reactivity data generated

are able to be readily combined with char structural data for assimilation into char conversion models.

2 Objectives

A previous ACARP/CRC project (C6052)¹ established facilities and developed techniques to perform bench scale evaluations of coal volatile yields and char gasification reactivities at elevated pressures. These techniques used a pressurised wire-mesh reactor to measure coal volatile yields and to produce devolatilised char samples, and a pressurised thermogravimetric analyser to measure the chemical reactivity of these chars under conditions relevant to advanced coal utilisation processes such as entrained-flow gasification and pressurised fluidised bed combustion/gasification systems. The data generated are of a form that allows them to be incorporated into transportable gasification models, making the assessment of Australian coals for use in advanced technologies less reliant on large-scale, expensive demonstration facilities.

The objective of the present work is to use these facilities to determine volatile yields and char gasification reaction rates of the CRC coal sample suite to O₂, CO₂ and H₂O at pressures of 15 atmospheres. This will provide a comparative database of a range of coals with ranks varying from sub-bituminous to semi-anthracite, aiding the development of coal performance models and hence the assessment of their use in advanced technologies.

3 Introduction

3.1 Australian Black Coals in Advanced Technologies

To assess and improve the performance of coals in advanced technologies, it is important to understand the sequence of reaction steps undergone by coal particles, and then identify which step or steps are rate limiting in the process. For example, in pf combustion and gasification, fine coal particles are injected into a high temperature environment where they undergo very rapid heating (in the region of 10^4 K/s) producing volatiles and a solid char residue. This volatile evolution and its subsequent combustion is rapid, hence, the rate of volatile evolution is not the rate-limiting step. The conversion of the solid char residue is much slower, and dictates the required residence time for coal in a combustor or gasifier.

The devolatilisation process, however, does impact strongly on the conversion rates of coals. Key amongst the factors that contribute to coal conversion is the amount of char remaining after devolatilisation and its physical structure (particle size, pore volume, pore surface area). The quantity of char and its structure depend, inter alia, on the amount and rate of volatile matter evolution. The reactivity of the char produced – especially under high temperature conditions – can also be affected by the pyrolysis conditions.

Advanced coal utilisation technologies, on which many new demonstration plants worldwide are based, operate at high pressures to increase reaction intensity and coal throughput. Whilst coal devolatilisation and char reactivity are relatively well understood at atmospheric pressure, the effects of increased pressure on coal volatile yields and char reaction rates are not well known. An understanding of these effects is required for coal assessment, reactor design and for the development and application of predictive coal and technology performance models. The measurement of volatile yields and chemical reaction rates of chars at elevated pressures are the focus of this report.

The advanced technologies that can take advantage of the data provided in this report are still under development or are at the demonstration stages only. It is therefore important to have an appropriate understanding of the coal performance issues and thus be able to better identify where more detailed coal technology performance information is likely to be required. This is particularly true for Australia where we have no direct involvement with the development or demonstration of these emerging technologies but will need to appropriately select and position Australian export coals within the energy market as these technologies emerge.

3.2 Measuring Coal Conversion Processes at Elevated Pressures

3.2.1 Coal Pyrolysis

It is well known that the amount, composition, and rate of evolution of volatile matter depend not only on coal type but also on the conditions of devolatilisation. The rate of heating (which depends on particle size as well as on surrounding temperature), atmosphere (oxidising, neutral, reducing), and absolute pressure all have an effect²⁻⁴. In particular, the volatile yield during the heating of fine coal particles at atmospheric pressure, is much greater (by 50 to 100%)^{5, 6} than that found during standard assay testing. There is, in fact, a large body of data on the volatile yield and kinetics for fine coal particles, under oxidising, neutral and reducing atmospheres, at temperatures from 500 to 1500°C^{2-4, 7, 8}. This body of data is extended by a strong, if as yet incomplete effort to model the pyrolysis process.

Data and modelling of pyrolysis at increased pressures, however, are sparse. What has been shown is that, when compared with atmospheric pressure testing, pyrolysis yields are strongly reduced at conditions of concern here (5 to 20 atm)^{4, 9}. Whilst there is no conflict in the small number of studies done, the measurements have been carried out with a small number of (non-Australian) coals over a very limited range of conditions^{2-4, 7, 8, 10}. There are no data that will allow an adequate estimate of coal devolatilisation, or of the properties of the resultant chars for the pyrolysis of Australian coals at elevated pressures.

The classical proximate analysis test for volatile matter (VM) provides data under a standard set of conditions. Unfortunately, these conditions do not truly reflect those found in advanced thermal conversion systems. It is possible to begin to simulate these process conditions in large scale pressurised entrained-flow or drop-tube facilities; however the installation, commissioning and operation of these facilities is usually expensive and time-consuming. Reasonably simple test procedures that suitably reflect conditions found in these systems are therefore required.

Experimental procedures have been developed in previous work¹ to measure coal volatile yields and produce chars under rapid heating rate, high-pressure conditions, using a bench-scale wire-mesh reactor (WMR). This facility and the results it has generated will be discussed in later sections of this report.

3.2.2 Char Reactivity

It has already been mentioned that the conversion of coal char produced after pyrolysis is the rate-limiting stage of coal combustion and gasification. The rate of char conversion is dependant on a number of factors. The 'intrinsic reactivity' of a coal char is one of these, and is an important consideration in the development of models to assess and predict coal performance under the complex reaction conditions present in most high temperature coal utilisation

technologies. For the purposes of this project, the intrinsic reactivity of a char is defined as the chemical reaction rate of the char measured under conditions where chemical processes alone control reaction rates, normalised to the measured surface area of the char. Under these conditions, effects of mass transfer of reactant or product gas, both within and external to the char particle, are removed by careful selection of reaction conditions. It is sometimes possible to extract intrinsic rate data from high temperature entrained flow reactor measurements through careful analysis of the data; however, this is a complex process for heterogeneous and porous particles reacting under the conditions found in pulverised coal combustion and gasification applications.

To be able to measure intrinsic char–gas kinetics at high pressures, we need to create reaction conditions under which chemical reactions are rate determining; that is, where gas diffusion rates within and external to the particle are much faster than the heterogeneous chemical reaction rates. This is best achieved by reacting small samples of chars with O₂, H₂O and CO₂ at relatively low temperatures. For O₂–char reactions this is typically below 450°C, and for the much slower CO₂ and H₂O reactions, temperatures below 900°C are generally suitable. These conditions have been found to be suitable for particles up to approximately 1 mm in size, enabling them to react in differential mode – that is conditions of excess gaseous reactant with negligible contribution of the product gases to the measured reaction rate.

At low temperatures such as these, the diffusion of reactant gases (both to the particle's external surface and through the pore structure of the particle) is much faster than the rate of chemical reaction at the char surface. Consequently, the rate of chemical reaction controls the rate of conversion of the char. This is defined as 'Regime I', or chemical reaction rate controlled regime¹¹. Here, the measured activation energy is the true activation energy and the measured reaction order is the true reaction order, and since the reaction proceeds uniformly throughout the char particle, particles reacting in this regime will demonstrate a reducing-density, constant-volume burning profile.

The equipment and the techniques developed in the aforementioned previous work¹ have demonstrated the ability to provide reliable fundamental information on char gasification reactivity. In particular, chemical reaction rates of chars reacting at high pressures of O₂, CO₂ and H₂O can be measured – subsequent sections of this report provide comparative reactivity data for a set of 13 Australian coal chars produced at high pressures in the WMR.

4 Experimental Procedures

The purpose of this report is to provide comparative gasification performance data for the CRC coal sample suite. A brief description of the techniques used in this work are given below.

- The wire-mesh reactor is a bench scale apparatus, able to provide coal volatile yields during pyrolysis under high pressures and high heating rates, and to produce char samples that are similar in nature to those produced in practical gasification processes.
- The pressurised thermogravimetric analyser (TGA) is able to determine gasification rate data for small samples of chars such as those produced in the WMR. The measurements made in the TGA provide chemical reaction rate data for chars reacting with CO₂, O₂ and H₂O.

The basic principles of operation for both the WMR and TGA are outlined below but full details of the commissioning and system development programmes (proof-of-concept) can be found in two PhD theses^{9, 12} as well as an ACARP report and paper^{1, 13} produced during the project.

4.1 The Wire Mesh Reactor

A bench-scale wire-mesh reactor (WMR) was used to devolatilise the coal samples. It is capable of heating a small sample of coal at high pressures and with high heating rates. Figure 4.1 and Figure 4.2 show a schematic diagram and photo respectively of the apparatus. The maximum operating pressure of the reactor system is 50 atm. The VY reported here were determined at 15 atm. The system includes the capability of collecting pyrolysis products (tars and gases) along with the residual char.

The WMR was designed so that the overall volume of the system, and the surface area on which tar might condense, was minimised. This made the tar collection process more effective. To ensure that the reactor was easy to clean and maintain, the reactor was constructed of 316 stainless steel.

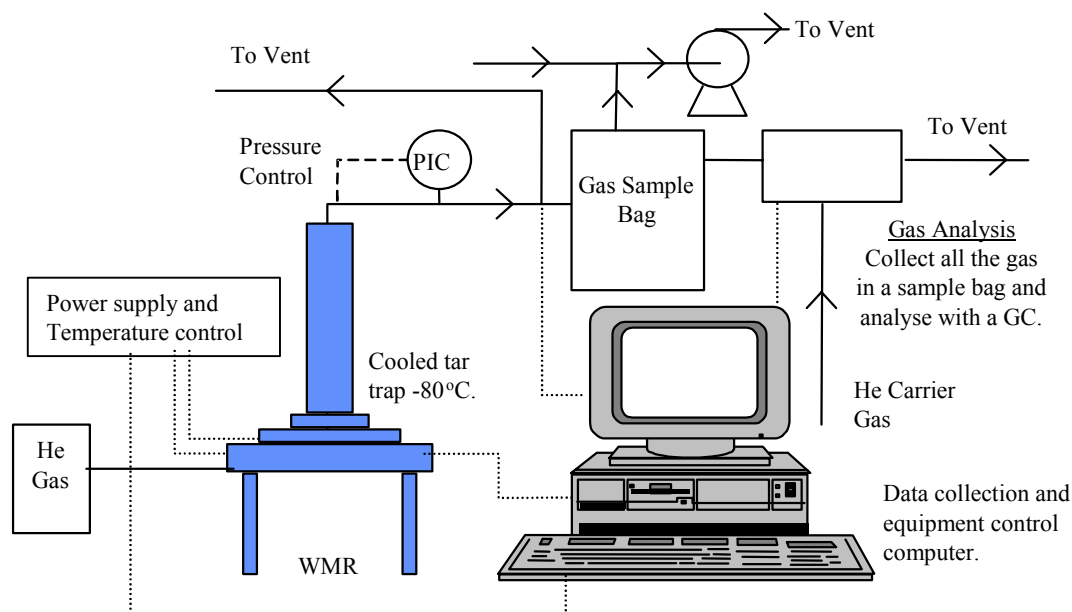


Figure 4.1 Schematic diagram of the wire-mesh reactor system.

The coal sample (~ 30 mg of $-150 + 106 \mu\text{m}$) is electrically heated by contact with the 316-grade stainless steel wire mesh. The specific dimensions of the mesh were 325 mesh ($44 \mu\text{m}$ openings) with a nominal wire diameter of $30 \mu\text{m}$. The mesh is held in the reactor between 2 brass terminal clamps. The coal sample is contained in a recess of approximately 15 mm diameter in the centre section of the folded mesh. Type K thermocouple wires were welded directly to the mesh to measure and control the mesh temperature. Mica insulators were used to electrically isolate the mesh from the reactor housing and also shaped to allow helium sweep gas to flow through the sample. Figure 4.3 shows a photograph of the mesh being heated with the reactor cover removed.

Ultra high purity helium sweep gas flowed through the reactor and through the sample to dilute and remove the evolved volatile material from the sample and to reduce the occurrence of secondary reactions of the volatile components that might be catalysed by prolonged contact with the hot sample or mesh. The evolved volatile material was swept from the hot zone of the reactor and then passed through a cooled tar trap before passing to the gas analysis system. A nominal flow rate of $5.5 \text{ L}_\text{N} \text{ min}^{-1}$ was used at all pressures to maintain a linear velocity of gas over the sample between 0.1 and 1.0 cm s^{-1} . Previous commissioning and testing of the WMR in this laboratory has shown this velocity to be sufficient to remove the volatiles before they undergo extensive secondary reactions on the heated mesh. The flow-rate was kept low enough to prevent excessive dilution of the gases prior to gas analysis.

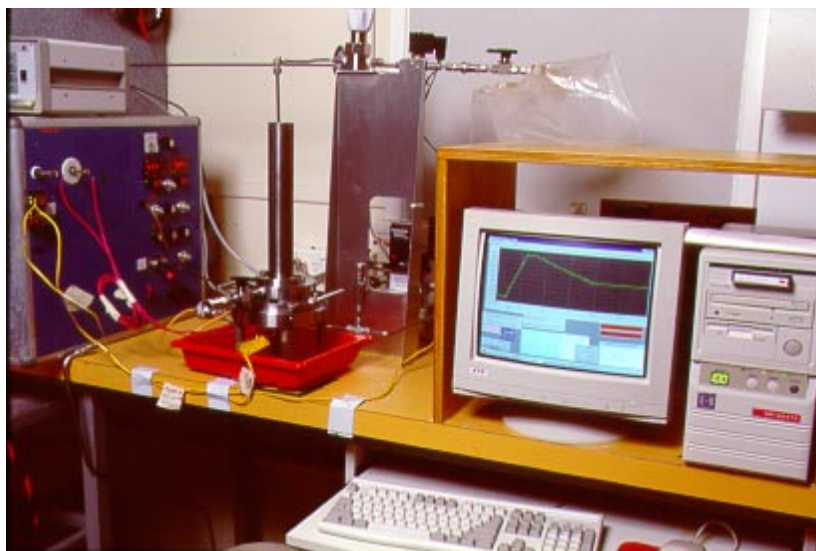


Figure 4.2: Photograph of the wire-mesh reactor system.

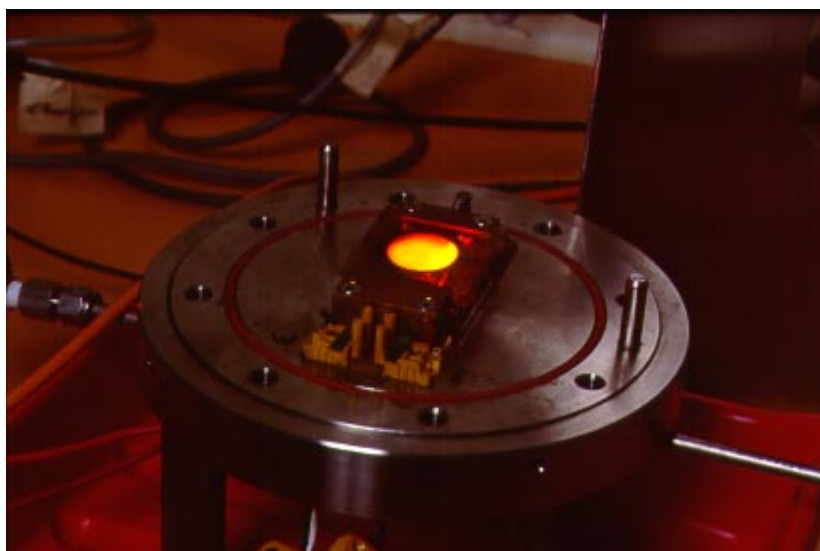


Figure 4.3: Photograph of the reactor being heated with the cover not in place

Initial tests were run employing mesh heating rates as high as 10^4 and 10^5 K/s. Tracing of the sample temperature relative to the mesh temperature at these higher heating rates indicated that the sample temperature lagged behind the mesh temperature. After extensive testing it was decided to perform the comparative study of the CRC coals under the following standard heating regime: room temperature to 1100°C at 1000 K/s and to hold the mesh and sample at this temperature for 10 seconds. This procedure provided reproducible results. Subsequently, the char sample was cooled down by the helium gas flow and the sample was removed for weighing and subsequent testing in the TGA.

Volatile yields were determined directly by weighing coal and char samples to a precision of 0.01 mg before and after the pyrolysis experiment. Char

samples were collected and used in characterisation studies performed in this and other projects.

It is also possible to determine the nature of the light gases and tars that evolve from the WMR procedure and thus provide a gas/tar/char breakdown.

4.2 Thermogravimetric Analyser

Reaction rate measurements at elevated pressures were performed in a thermogravimetric analyser, similar to one described in the literature¹⁴. This apparatus is fully described in a recent ACARP report¹ and an associated PhD thesis¹². This apparatus allows measurements of char-gas reaction rates at pressures up to 100 atm and temperatures up to 1100°C in atmospheres of oxygen, carbon dioxide and/or steam, diluted with either helium or nitrogen. A schematic of the reactor is presented in Figure 4.4.

The central component of the TGA system is a helium-purged microbalance. A chain connected to the microbalance arm suspends the char sample in a resistance-heated furnace through which the reactant gases flow. The sample is contained in a mesh basket constructed from Incoloy 800 with a mesh size of 100 μm . The maximum mass that can be suspended from the balance arm is 15 g. This allows the use of samples of up to approximately 4 g. Generally, it is not necessary or desirable to use samples of more than approximately 100 mg. The sample holder is connected to a winch mechanism that enables it to be raised from or lowered into the reaction zone. Extensive testing has verified that the range of sample masses and particle sizes used in this study did not impact on the reactivity data gleaned from this TGA set-up. Further details can be found in the ACARP report referred to earlier¹.

The temperature of the sample is measured using a thermocouple situated a few millimetres below the sample holder when in the lowered position. By keeping sample sizes small and reaction rates sufficiently slow both the sample and the thermocouple are situated within an isothermal zone and reaction thermodynamics do not alter the measured sample temperature significantly.

Gas flows are controlled by mass flow controllers with nominal maximum flow rates of 10 $\text{L}_\text{N} \text{min}^{-1}$ for the reactant gases and 20 $\text{L}_\text{N} \text{min}^{-1}$ for the purge gas. The reactant gases are preheated through two stages: the first stage is to 300°C (prior to entering the reactor) and the second stage is to the furnace temperature (prior to encountering the sample).

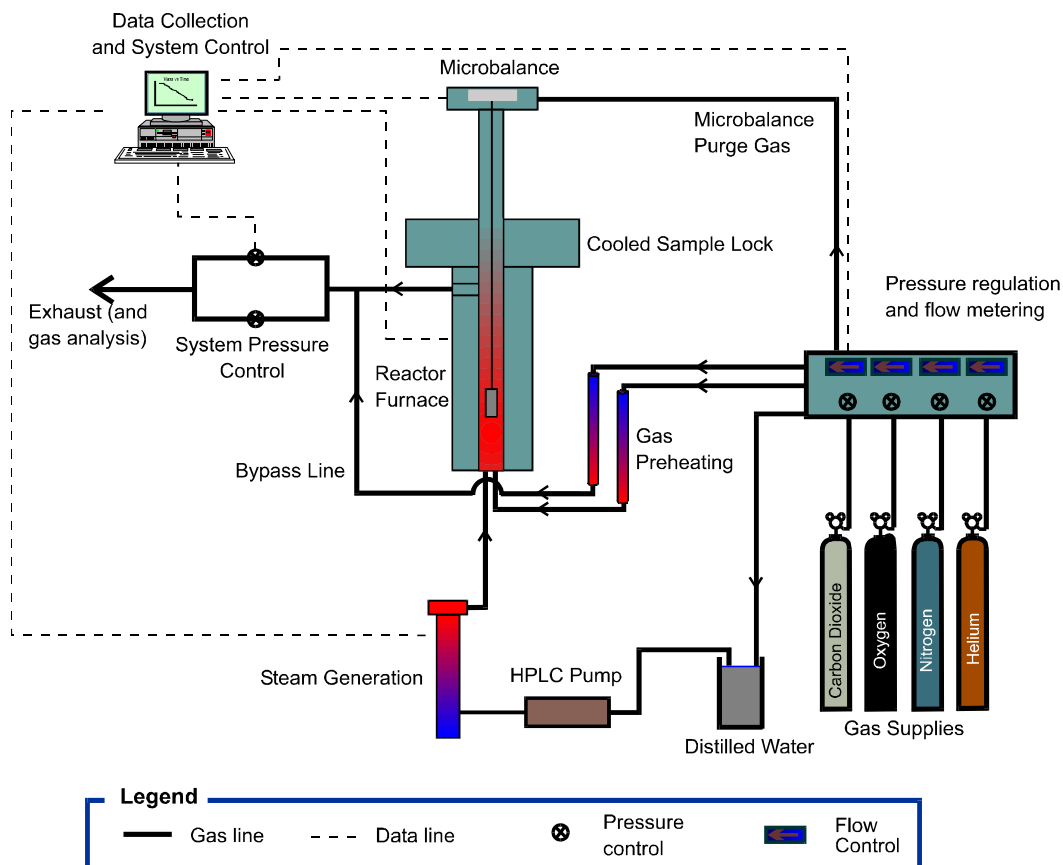


Figure 4.4: A schematic of the pressurised TGA apparatus

Pneumatic valves enable instantaneous switching of reactant gases from a bypass line to the line flowing through the reactor. The composition of the reactant gas can therefore be varied during an experiment.

System pressure is maintained by one of two computer-controlled back-pressure regulators; one used for high flow rates (lower pressures, up to approximately 30 atm) and the other for low flow rates (higher pressures, above approximately 30 atm).

A typical experiment is performed as follows. An air-dried (at 110°C) char sample was weighed and placed in the sample holder. This was then sealed into the water-cooled sample lock of the TGA. The reactor was heated to the reaction temperature and the system was pressurised to the required pressure using helium. The flow of reactant gas through the reactor was initiated when the system was close to the desired reaction pressure.

Once system pressure, gas composition and reactor temperature had stabilised, data acquisition was initiated and the sample was lowered into the furnace. During the course of an experiment, the sample temperature, sample mass and system pressures were recorded at preset time intervals. It was also possible to heat the sample to the reaction temperature in the furnace in an inert environment of helium or nitrogen, and switch this gas stream to the

reactant gas to initiate the reaction. Either method could be used to generate repeatable results; however, the first method was employed for all tests described here as it minimised the period in which the reactant gas composition was changing.

When the desired level of conversion had been achieved, the sample was removed from the reaction zone and cooled in the upper portion (water-cooled) of the apparatus that was flushed with helium. The reactor was then depressurised and the sample removed and weighed.

Verification testing had been completed prior to this set of experiments to ensure the reaction was conducted under Regime I kinetic conditions and that neither particle size, sample mass or gas flowrate had no significant effect on the measured rates.

The mass, temperature and pressure data were evaluated post-experiment using a custom software package. The calculations considered sample buoyancy, sample holder drag and the effects of pressure and temperature on the balance reading. The recorded data (mass vs time) were corrected for these effects. The primary data is a chart of apparent reaction rate as a function of conversion. An example of a typical result from the TGA is shown in Figure 5.10.

Indices used to compare the reactivities of the samples included carbon conversion (X), defined as:

$$X = \frac{w_0 - w}{w_0} \times 100 \quad \% \quad (1)$$

where w_0 is the initial mass of the sample (on a dry, mineral matter-free basis) and w is the mass of the sample after gasification (on a dry, mineral matter-free basis). The apparent reaction rate (r_a) of a sample is calculated from the TGA data using the equation:

$$r_a = -\frac{1}{w} \cdot \frac{dw}{dt} \quad \text{g g}^{-1} \text{ s}^{-1} \quad (2)$$

In this equation, w is the instantaneous mass of carbon remaining in the sample (on a dry, mineral matter-free basis) and dw/dt is the rate of mass loss. Thus the units are 'grams of carbon reacting per grams of carbon remaining per second'. To convert this rate to an intrinsic rate, it is necessary to divide the apparent rate by the total surface area of the particle, measured by either N_2 or CO_2 adsorption. A detailed account of the TGA operating and data processing procedures can be found elsewhere¹.

4.3 Surface Areas

As part of the characterisation of the coals and their chars (before and after reaction) total surface areas of the particles were also determined. These were performed using two techniques. One was adsorption of nitrogen at 77 K and subsequent interpretation using the BET isotherm, and the other was adsorption of CO₂ at 273 K and data manipulation using the Dubinin-Astakhov relationship.

Each of these techniques provides information of a different 'type' of surface. The N₂ technique characterises the meso (2 to 50nm diameter) and macropore surface area of a particle (pores generally larger than 50nm diameter) and the CO₂ technique includes the micropore surface area (pores generally under 2nm). Thus a sample with a large CO₂ area and a small N₂ area can be said to have an extensive micropore network, whilst a large N₂ area is indicative of an extensive meso- and macroporous structure.

5 Results

5.1 Volatile Release Data

The volatile yield (VY) data presented in this section of work are obtained from experiments performed on the CRC coals at 15 atm using standardised conditions determined in the previous section.

Figure 5.1 below shows previous results obtained using the WMR discussed in this work compared with data from similar work by others using a range of international coals ^{2, 4, 7, 8, 15, 16}. Volatile yields have been shown to decrease with increasing pressure. Furthermore, VY data have been collected under vacuum conditions and these give volatile yields up to 10 wt% on the coal higher than standard proximate VM values.

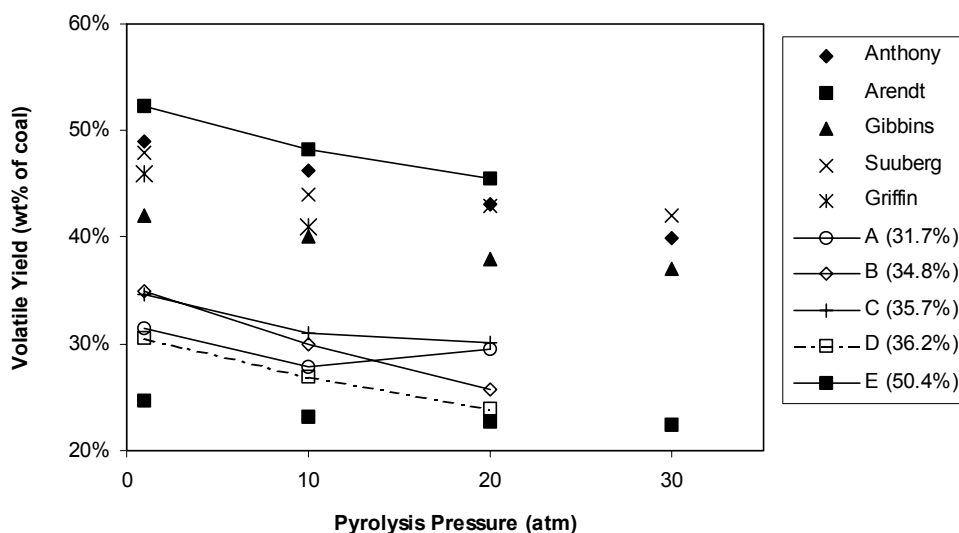


Figure 5.1: Volatile yields vs pressure for several coals (with prox. VM shown in parentheses), comparing results from the WMR method developed in the PhD thesis⁹ with other pressurised pyrolysis data. Data connected by lines are generated in the present work and the data plotted as points are from the literature.

Figure 5.1 shows that some coals have demonstrated that increasing pyrolysis pressure from 1 atm to 20 atm decreases volatile yields by up to 10.5wt% of the volatile yield measured at 1 atm⁹. In this work, the magnitude of the decrease did not appear to be correlated directly with coal rank. Based on analysis of the evolved gas and other volatiles, most of the decrease in volatile yield was attributed to less tar being produced at higher pressure.

Figure 5.1 also shows how VY at high heating rates can be greater than the proximate VM reported for a coal at 1 atm. As the pressure increases, VY decreases and at high pressures, become less than the proximate VM value for that coal. Previous work by Smith et al.¹⁷ as part of NERDDC project 1110, tested a variety of Australian low volatile coals in a drop tube furnace at 1 atm and found that their VY were significantly enhanced relative to their proximate VM values. This coincides with other work on high volatile coals which indicates an enhancement of VY when high heating rates are employed at 1 atm³. Thus there are two factors to consider when assessing the potential difference between VM assaying and actual volatile yield: the enhancement of the VY resulting from the increase in heating rate, and the inhibition of volatile matter evolution resulting from the increase in pressure.

Figure 5.2 shows the comparison between the proximate volatile matter (VM) and the volatile yields (VY) for all CRC coals, using data generated in the current project. These data were generated using the WMR heating at 1000°C/s to 1100°C with a total pressure of 15 atm. The coals are presented in an approximate lowest to highest rank order from left to right across the chart. It is suggested here that there is a rank related trend in volatile yield for these coals. Broadly speaking, lower rank coals (such as CRC 252) generate somewhat greater VY under these conditions when compared to their proximate VM values. High volatile bituminous coals at 15 atm produce VY similar to the VM, while semi anthracite (lower VM) coals like CRC 281 show significant reductions in their VY relative to their proximate VM. Simply put, this figure shows that the effect of pressure on decreased VY is greater for higher rank coals.

As mentioned, this comparison was made at 15 atm total pressure. Based on the data presented in Figure 5.1, it is apparent that at a higher pressure the reduction in VY is expected to be greater. Thus these data do not represent the maximum decrease expected in VY from pyrolysis at increased pressures in gasification and combustion applications.

It was not possible to provide volatile yield data for the high volatile CRC coal 297 (VM = 51% daf) as the volatile evolution process during the WMR testing was so violent as to result in meshes that were consistently blown apart. Modifications are being made to the sample size and experimental procedures to enable determination of volatile yields of very high volatile coals.

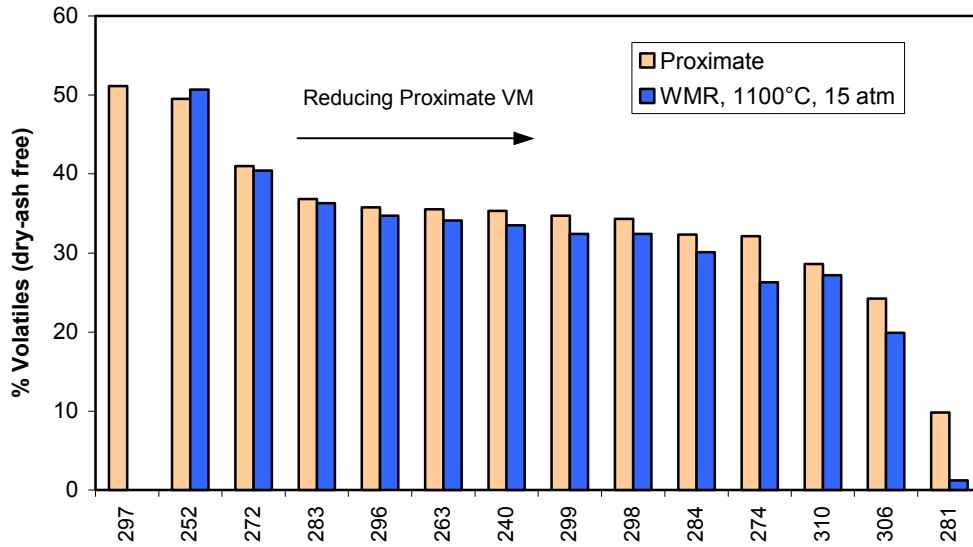


Figure 5.2: Comparison of the proximate VM and WMR volatile yield data for all 14 CRC coals at 15 atm and 1100°C.

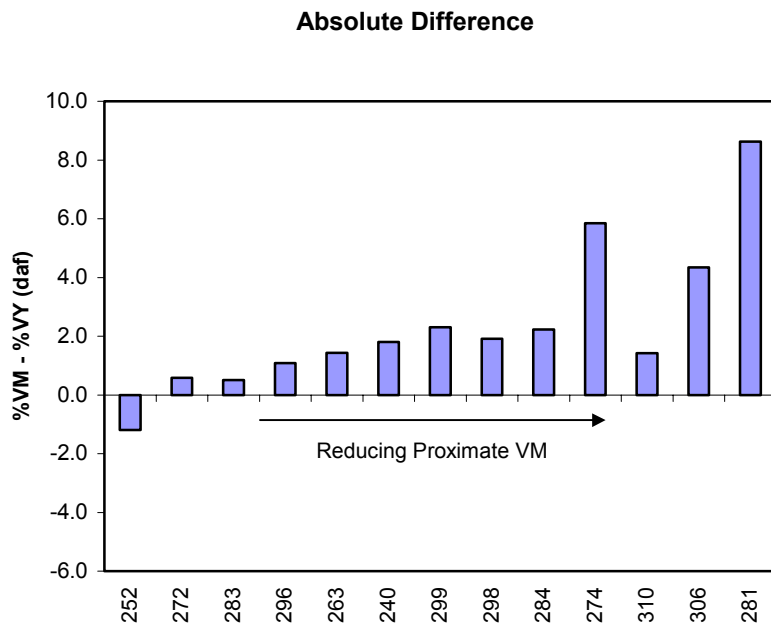


Figure 5.3: Absolute difference between proximate VM and VY from WMR experiments

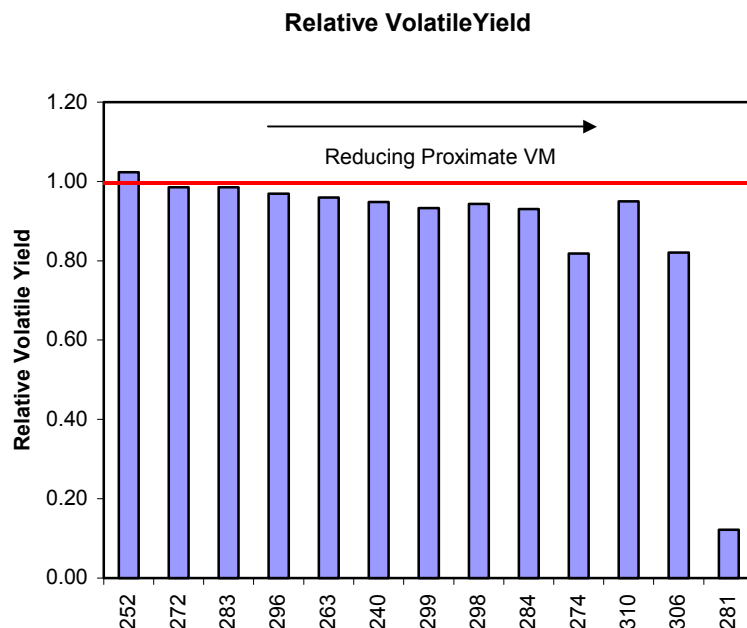


Figure 5.4: Relative Volatile Yield for each coal. i.e. The VY divided by VM. The red line represents the unity values for VY and VM.

Figure 5.3 displays the data presented in Figure 5.2 in an ‘absolute difference’ format (the difference between the VM% and the VY%) and Figure 5.4 displays these data as relative volatile yields (the relative volatile yield is defined as $(VY\%(daf)/VM\%(daf))$). Previous work at 1 atm indicates that most coals produce a significantly greater VY at higher heating rates than their proximate VM would suggest. In the case of the high volatile coal (252) evidence of this enhanced volatile yield is still present even at 15 atm. As mentioned, it would be expected that at higher pressures the VY would decrease further. All other coals examined here have VY less than the proximate VM at pressures of 15 atm. It has been shown that their VY at 1 atm would exceed their proximate VM values by anything from 1.1 to 1.7 times¹⁷.

There has been little work comparing bench-scale data (obtained from a WMR) with data from other experimental techniques, even at 1 atm. Hindmarsh et al.⁶ made some comparisons with WMR results and data from an entrained flow reactor (EFR). They concluded that for high rank coals the volatile yields are very similar for both the WMR and the EFR; however, for lower rank coals the volatile yields from the WMR were somewhat higher than that attained using the EFR.

Figure 5.5 shows volatile yields for CRC coals 263 and 272 as determined using the WMR and a drop tube furnace (as part of an associated project¹⁸) as a function of pressure. It can be seen here that the measured volatile yields did not differ significantly between the two techniques, thus providing some validation for this experimental technique.

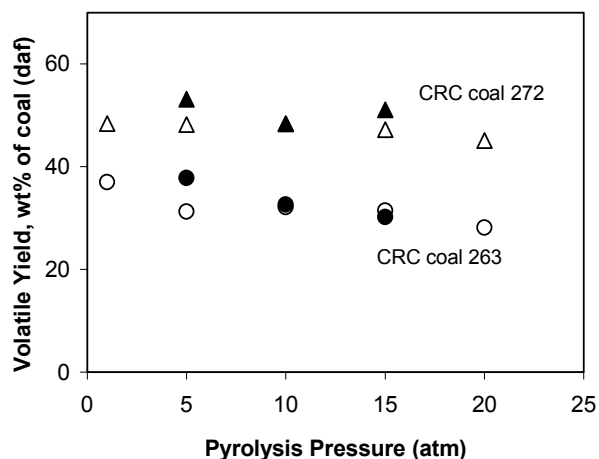


Figure 5.5: Comparison of volatile yields of CRC coals 263 and 272 following pyrolysis in the WMR and the PDF. Close symbols = DTF samples and open symbols = WMR samples. Triangles = CRC coal 272 and circles = CRC coal 263. Data obtained from¹⁸.

On the basis of the volatile yield results, the volatile yields of higher volatile coals, relative to their proximate volatile matter content, are seen to be less affected by increased pressure and hence could be seen to have some possible advantages over higher rank coals for technologies that employ elevated pressures and high heating rates as part of their energy cycle.

Overall, this comparison process demonstrates that under practical gasification conditions, where elevated temperatures and pressures exist, there can be significant differences between the proximate VM test predictions and the actual yield of volatile material. Specifically, coals such as 274, 306 and, quite noticeably, 281 have VY that are strongly suppressed at elevated pressures while coal 252 has a VY that is less affected by pressure and still achieves VY greater than the proximate VM at 15atm pressure.

5.2 Char Surface Areas

Figure 5.6 shows both the initial N₂ and CO₂ surface areas for all chars produced by devolatilisation in the WMR. All the chars have very low N₂ surface areas in the range 1–8 m² g⁻¹ while the CO₂ surface areas are in the range 160–332 m² g⁻¹. Higher CO₂ surface areas (especially when accompanied by lower N₂ surface areas) generally indicate a large micro porous structure¹⁹.

This can be attributed to the temperature at which the CO₂ adsorption test procedure is performed. The CO₂ adsorption is conducted at much higher temperature (248 K) than the N₂ adsorption (196 K). This gives the CO₂

molecules a higher average kinetic energy, enabling further penetration into the microporous structure. Thus, large N₂ surface areas indicate significant meso and macro porous structure. Based on these assumptions it would seem that these initial chars (low N₂ surface areas and high CO₂ surface areas) may have 'bottle-neck' pores¹⁹. These pores, as the name implies, exhibit 'bottle-neck' like openings and expand internally to provide the larger surface areas reflected in the CO₂ results. Tabulated data from Figure 5.6 are summarised in Table 5.1. The CO₂ surface areas were used to calculate intrinsic reaction rates from the apparent reaction rates measured using the TGA. These data are discussed in the next section.

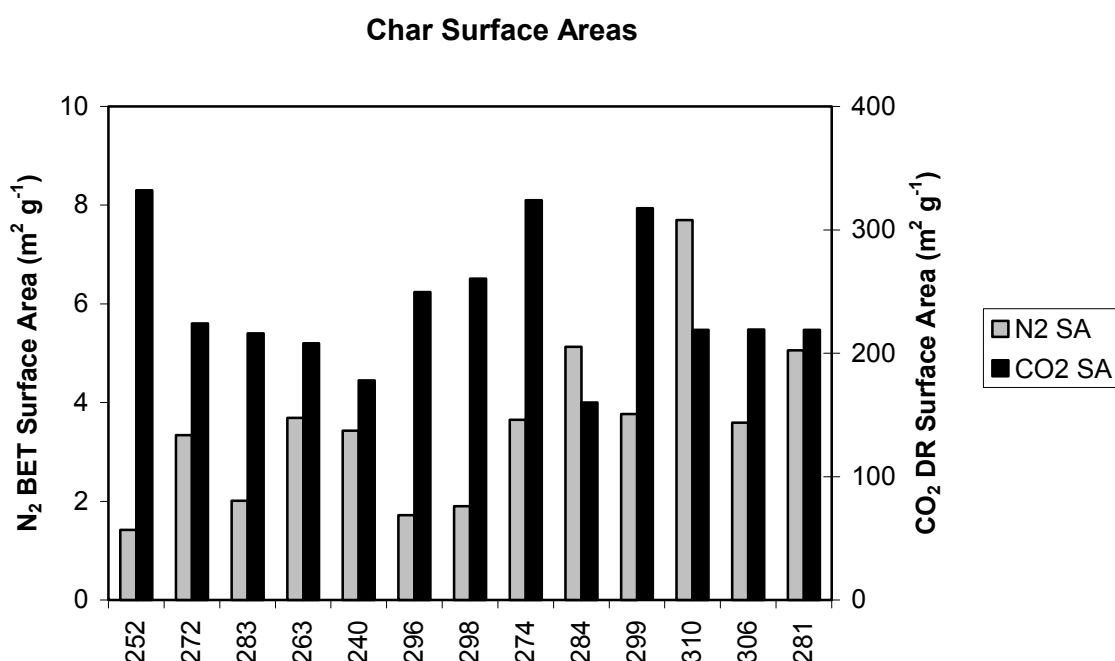


Figure 5.6: Initial chars surface areas produced in the WMR (both N₂ and CO₂)

CRC No.	N ₂ SA	CO ₂ SA	N ₂ SA	CO ₂ SA	N ₂ SA	CO ₂ SA	N ₂ SA	CO ₂ SA
			CO ₂	CO ₂	H ₂ O	H ₂ O	O ₂	O ₂
	(initial)	(initial)	(Converted)	(Converted)	(Converted)	(Converted)	(Converted)	(Converted)
	(m ² /g)	(m ² /g)	(m ² /g)	(m ² /g)	(m ² /g)	(m ² /g)	(m ² /g)	(m ² /g)
252	1.42	332	434	496	450	489	379	476
272	3.34	224	279	459	294	373	158	590
283	2.01	216	258	343	353	429	244	335
263	3.69	208	423	434	487	451	288	463
240	3.43	178	342	348	301	345	136	271
296	1.72	250	404	531	336	434	327	616
298	1.9	261	389	492	349	453	201	346
274	3.65	324	396	530	385	556	55	191
284	5.13	160	205	273	271	347	165	268
299	3.77	317	444	488	353	460	195	275
310	7.7	219	216	323	199	370	205	345
306	3.59	219	234	363	300	373	133	223
281	5.06	219	455	608	422	587	71	206

Table 5.1: N₂ and CO₂ surface areas for all chars tested both initial and at 25% conversion (“converted”).

Table 5.1 shows an interesting relationship between N₂ and CO₂ surface areas. Initial N₂ surface areas are always greatly lower than the CO₂ surface areas. This indicates, as discussed in a previous section, that the chars produced in the WMR have significant micro-porous structure. Subsequent reaction in CO₂, H₂O and O₂ apparently result in an opening-up of the char pore structure in most samples as demonstrated in the N₂ and CO₂ (at 25 % conversion) and creating larger surface area pores in the meso to macro porous range. The N₂ and CO₂ surface areas converge to similar values as the chars are reacted.

Figure 5.7, Figure 5.8 and Figure 5.9 show the comparative changes in both the initial char surface area (N₂ and CO₂ areas) and that after partial gasification (25% wt loss) of the char for all chars tested in these experiments. In Figure 5.7 the N₂ surface areas converge with the CO₂ surface areas of the chars reacted with CO₂. The O₂ reacted chars exhibit significantly higher CO₂ surface areas relative to the N₂ values (on average ~100 m² g⁻¹) except for sample 252, a subbituminous coal sample which would indicate that the initial and reacted pore structures were more meso to macro porous in nature. Sample 274 has an initial CO₂ surface area greater than the reacted CO₂ surface area indicating significant macro porous development in this sample as a result of its reaction with O₂. Samples 306 and 281 have similar CO₂ surface area for both initial and reacted samples indicating relatively little change in pore structure with reaction.

Unreacted and CO₂ Reacted Char Surface Areas in N₂ and CO₂

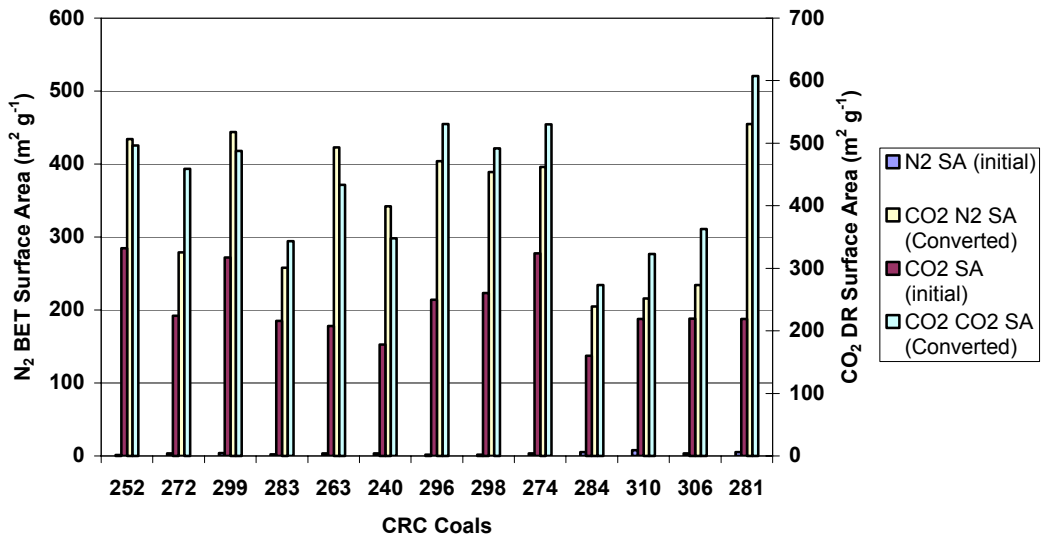


Figure 5.7: Initial N₂ and CO₂ surface areas along with CO₂ reacted char surface areas in N₂ and CO₂.

Unreacted and H₂O Reacted Char Surface Areas in N₂ and CO₂

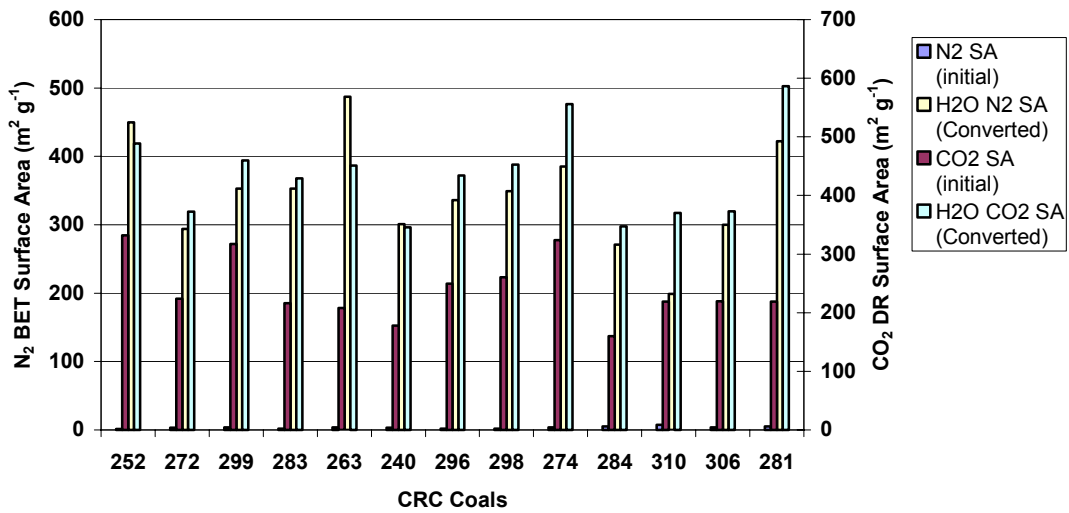


Figure 5.8: Initial N₂ and CO₂ surface areas along with H₂O reacted char surface areas in N₂ and CO₂.

Unreacted and O₂ Reacted Char Surface Areas in N₂ and CO₂

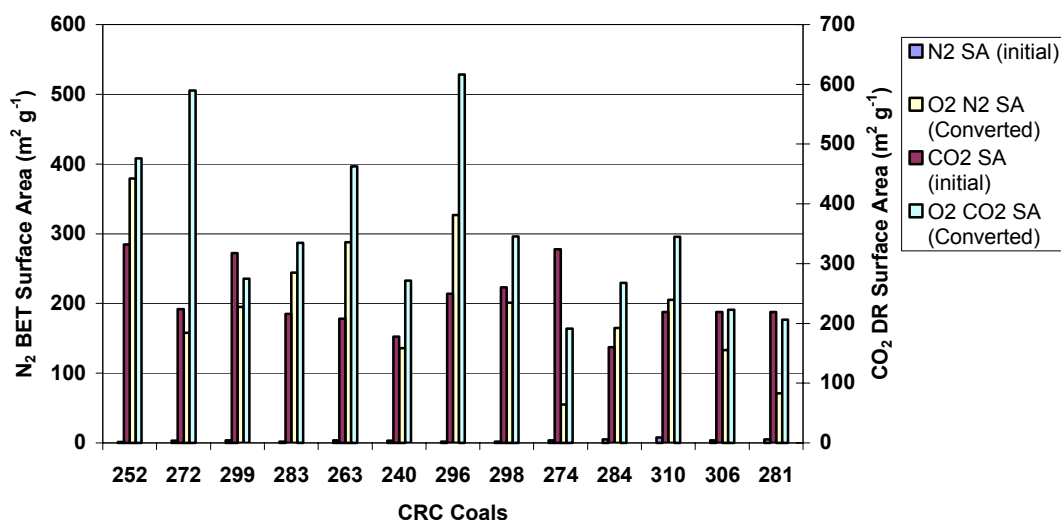


Figure 5.9: Initial N₂ and CO₂ surface areas along with O₂ reacted char surface areas in N₂ and CO₂.

5.3 Char Reactivity Measurements

This section presents the results from reactivity measurements utilising the pressurised TGA apparatus. All chars were reacted in 100% CO₂, 50% O₂ in N₂ and 100% H₂O at 900, 300 and 800°C respectively. These results are shown in graphical form as apparent and intrinsic reaction rates of the fresh char (0% conversion) and apparent and intrinsic reaction rates at (generally) 25% conversion. In some instances, practical limitations of the reactor system resulted in slightly less than 25 % char conversions. However, after consideration of the rate vs. conversion profiles for these chars it was considered further reaction (up to another 10 % conversion) would result in little change in the overall reaction rates. Thus, should critical evaluation of the data presented in this report be required, due consideration should be given.

Plots of reaction rate vs. conversion for all the chars tested are presented in Figure 5.10, Figure 5.11 and Figure 5.12 for reactions with CO₂, H₂O and O₂ respectively.

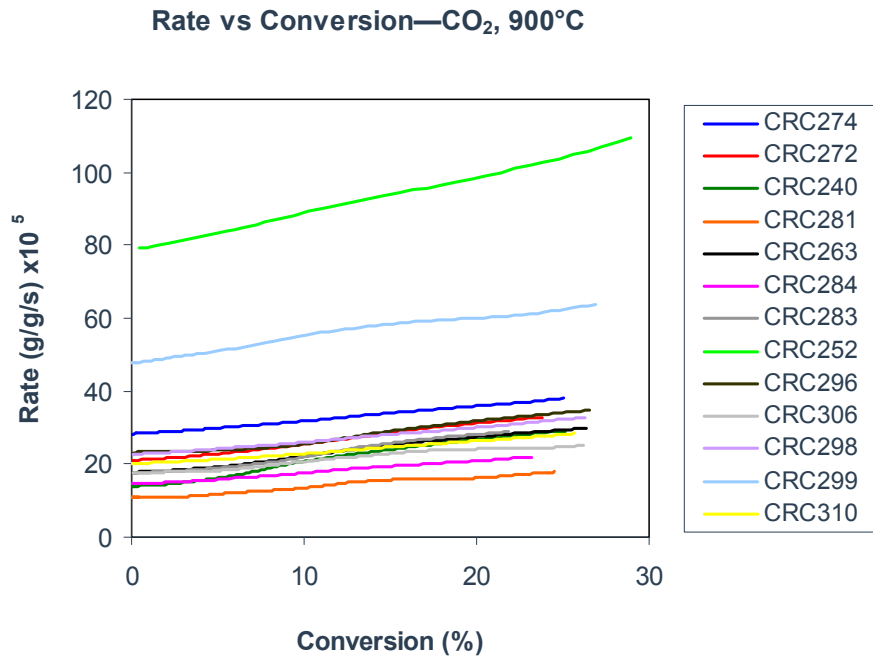


Figure 5.10: Rate vs conversion profiles for all CRC chars tested in 100% CO₂ at 900°C and 15 atm

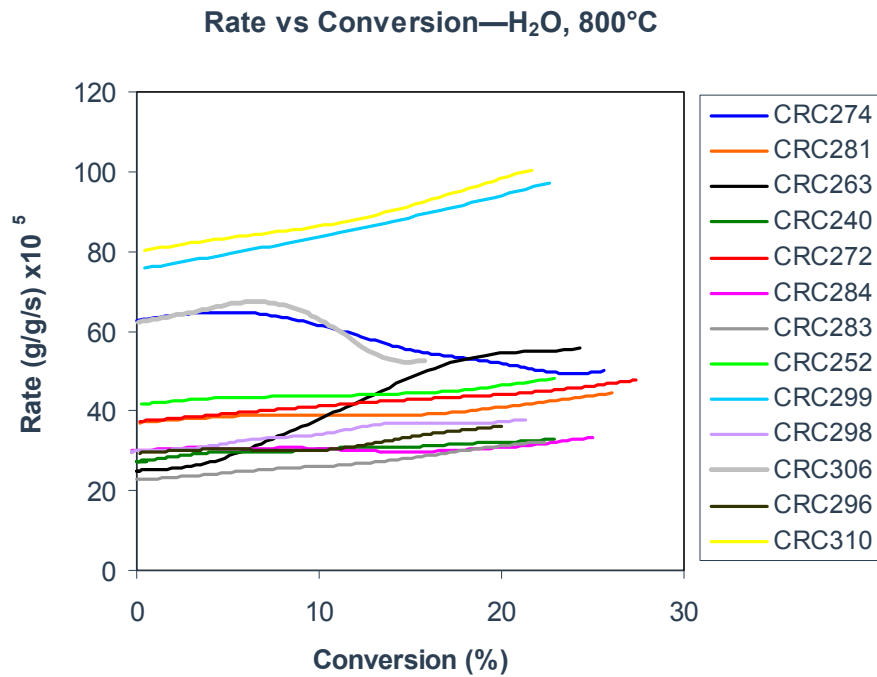


Figure 5.11: Rate vs conversion profiles for all CRC chars tested in 100% H₂O at 800°C and 15 atm

Rate vs Conversion—O₂, 300°C

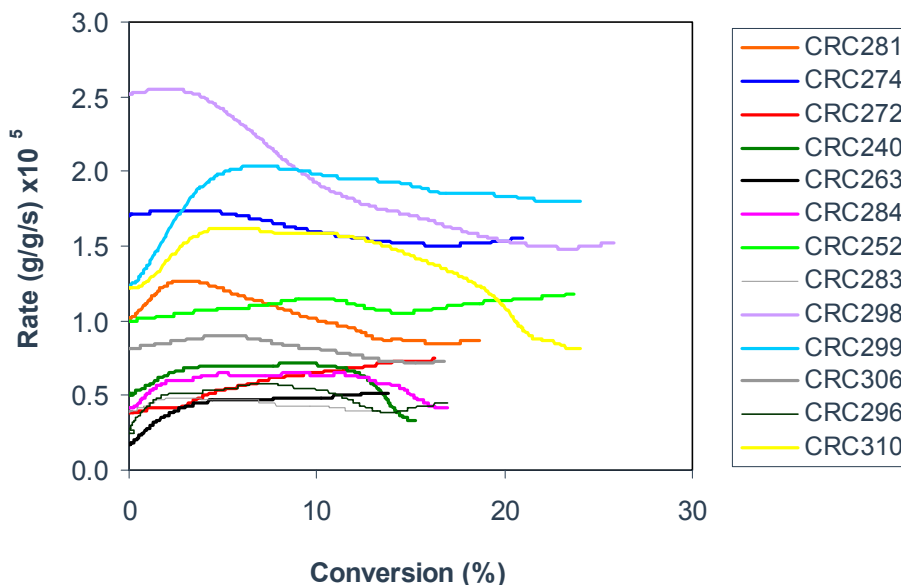


Figure 5.12: Rate vs conversion profiles for all CRC chars tested in 50% O₂ at 300°C and 15 atm

It can be seen from the above three conversion profiles that reaction with CO₂ produced similar shaped traces for all chars: reaction rates increased consistently with increasing conversion. Reactions with steam show similar steadily increasing rates with conversion except for samples 274 and 306 where the reaction rate began to decrease after approximately 4 to 5% conversion. Reaction with O₂ showed initially increasing reaction rates for all samples to ~4% conversion with most chars showing decreases in reaction rates at higher conversion levels. The exceptions here were chars made from coals 252, 272 and 263.

Figure 5.13 to Figure 5.18 below show the comparative reaction rates for all CRC chars tested. These include apparent and intrinsic rates at zero and 25% conversion levels in CO₂, H₂O and O₂. Note that the scales on both reaction rate axes are different. The intrinsic reaction rates (g/m²/s) were calculated from the measured reaction rates and the CO₂ surface areas reported in Section 5.2. These bar charts show quite effectively the impact of normalising the apparent rates to the surface area characteristics of each char tested. The CO₂ reactivity results in particular show how surface area can account for a lot of the observed inter-char variations in apparent reaction rates – this effect is not as noticeable in the O₂ and the H₂O results. This is discussed in more detail both later in this section and in the Discussion section of the report.

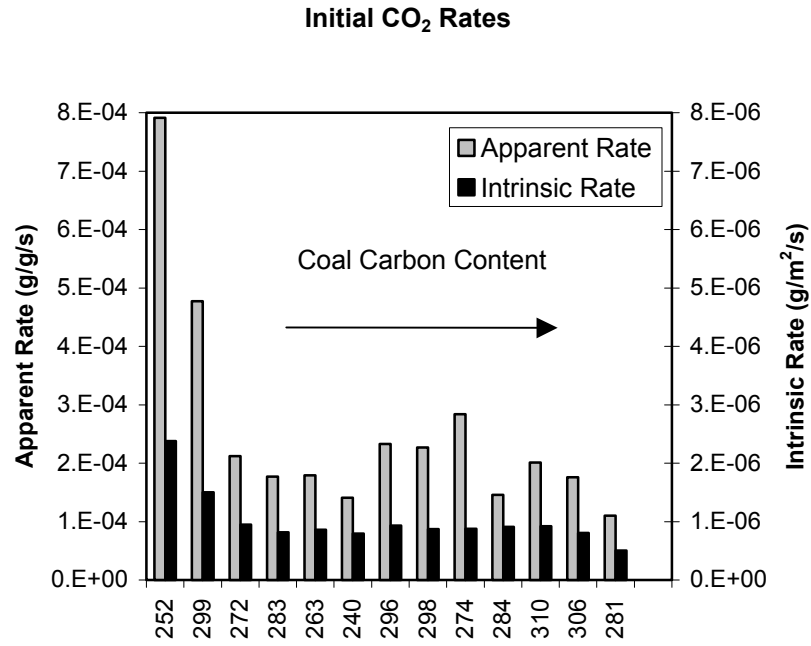


Figure 5.13: Apparent and intrinsic CO₂ reaction rates (initial) for all CRC chars tested

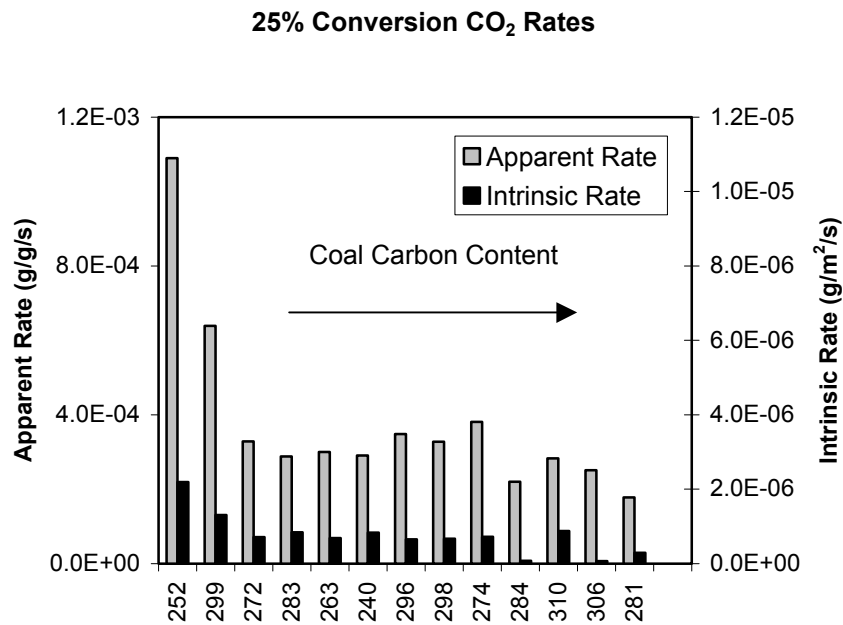


Figure 5.14: Apparent and intrinsic 25% conversion CO₂ reaction rates for all CRC chars tested

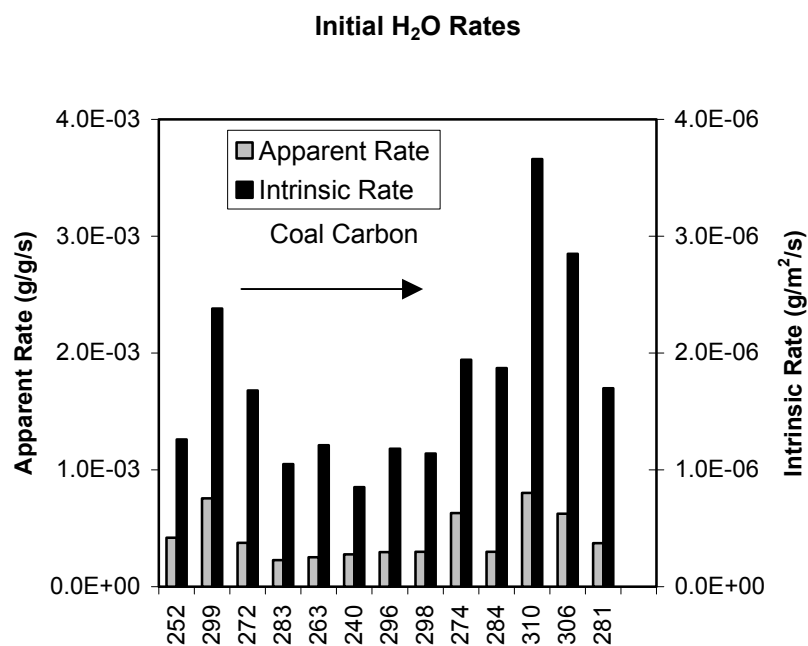


Figure 5.15: Apparent and intrinsic initial H₂O reaction rates for all CRC chars tested

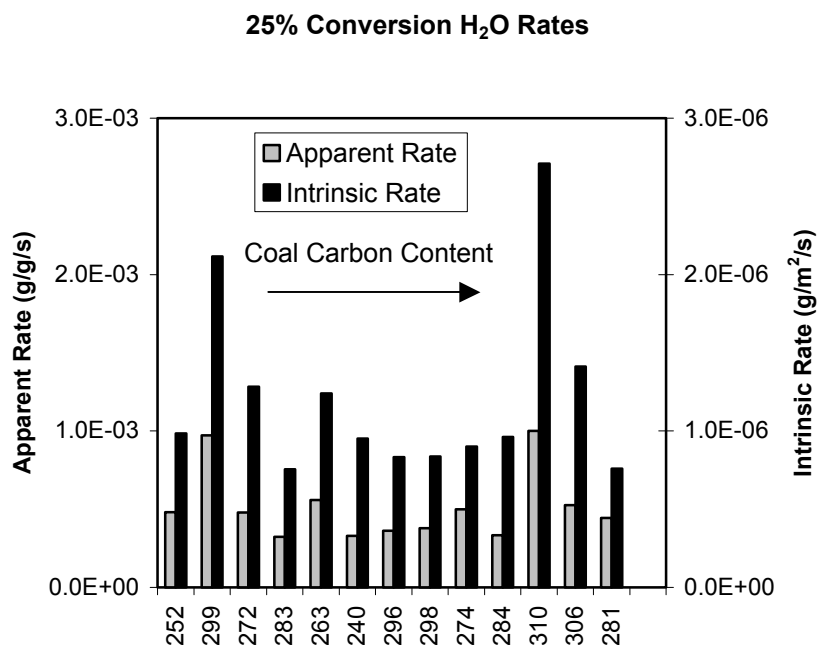


Figure 5.16: Apparent and intrinsic 25% conversion H₂O reaction rates for all CRC chars tested

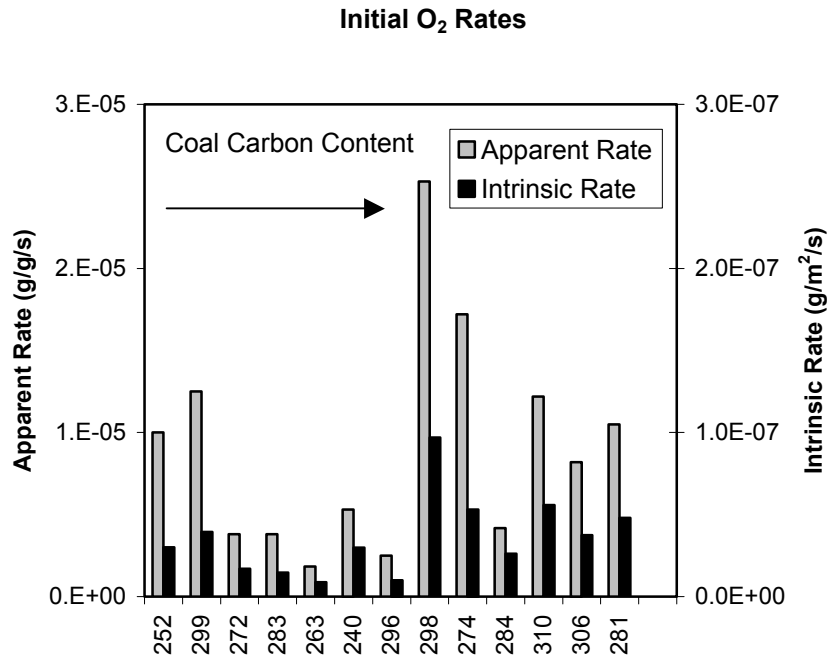


Figure 5.17: Apparent and intrinsic initial O₂ reaction rates for all CRC chars tested

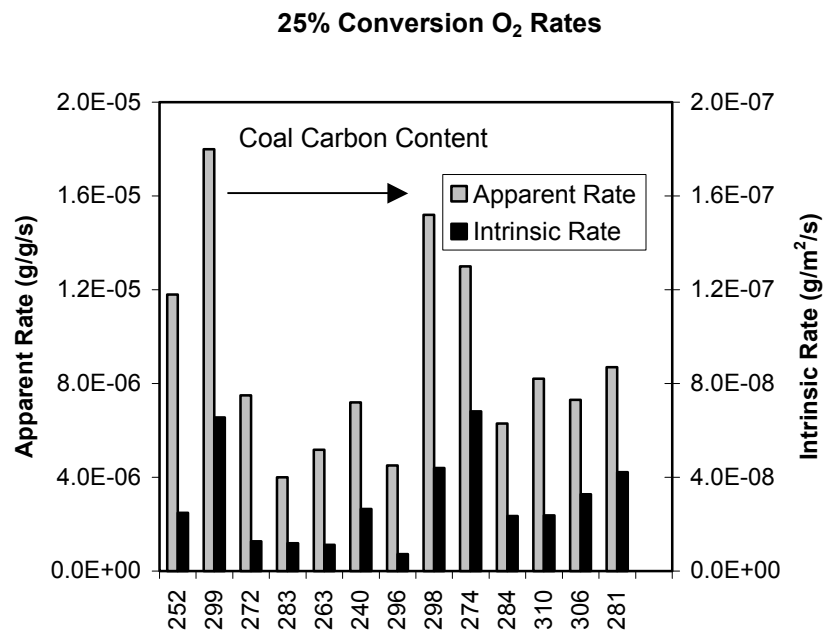


Figure 5.18: Apparent and intrinsic 25% conversion O₂ reaction rates for all CRC chars tested

A few points should be made prior to discussing the results provided above. Samples 252 and 299 are subbituminous coals and sample 281 is a semi-anthracite. All other samples are of similar rank and would be defined as bituminous. It should also be noted that the char samples in this section of work are presented in carbon content or coal rank order not in order of volatile content as indicated in previous charts.

Figure 5.13 shows initial reaction rate data in CO₂, which indicate a relatively consistent apparent reaction rate (in the order of 1.5 to 3.0×10^{-4} g/g/s) for all chars tested here with the exception of 252 and 299 which are showing significantly higher rates – in some instances 3 to 4 times that of the initial apparent rates of the bituminous coal chars. As mentioned, these chars are prepared from sub-bituminous coals. When surface areas are considered, the intrinsic rates show much less variation between char samples. The exceptions are chars made from coals 252 and 299 which, again, are lower rank coals. This indicates that for the higher-ranked coals in this set, surface area is a major contributor to determining the apparent reaction rate in CO₂.

These trends are repeated for the data obtained after 25% conversion (Figure 5.14). There are still some inter-char variations in intrinsic reaction rates – this indicates that, for reactions under CO₂ conditions, surface area alone does not fully account for the observed differences between chars. Catalytic effects of mineral constituents and varying degrees of char crystallinity are likely to be important contributors to the remaining variations between intrinsic reaction rates for char samples reacting with CO₂. Furthermore, the potential for catalytic effects to be significant appears to be greater in those chars made from lower-ranked coals. This is consistent with the large amount of literature in this regard which indicates that, for higher-ranked coal chars reacting in CO₂, surface areas tends to be more significant to the measured rate than the catalysis of mineral matter; and conversely, for lower-ranked coal chars reacting in CO₂, the effects of catalysis by finely dispersed, organically-bound mineral matter are likely to be greater.

The H₂O reactivity data (Figure 5.15 and Figure 5.16) exhibit different trends to the CO₂ results shown above. The reaction rates do not appear to have any rank dependence. The initial apparent char reaction rate data show more variation between coals than the CO₂ data – in this case a factor of 4 difference between the slowest and the fastest apparent rates. Also unlike the CO₂ data, these variations were not largely accounted for upon normalisation to the char surface area, indicating that for these chars other factors (mineral matter, crystallinity etc.) are significant. The data at 25% conversion show similar trends to the initial rate plots, in that there is still a factor of 4 difference in the variation between coal chars, and that these relative rates are largely unchanged upon normalisation to the char surface area. There is also no rank effect noticeable in the intrinsic rate data.

Figure 5.17 and Figure 5.18 show the O₂ reaction rate data (both apparent and intrinsic). Again, there are no coal rank trends in either the apparent or

intrinsic data. Inter-coal variations on an initial apparent rate basis was up to 14 times while the 25% conversion data shows a reduction down to approximately 5 times. However, the intrinsic rate data for both plots shows variations across samples of some 4 times while the 25% conversion results show variations of approximately 3 times. This indicates that surface area is an important contributor to the observed rate variations between coals, but that factors other than surface area alone (things such as mineral constituents and crystallinity) also contribute to these variations in reaction rate.

To fully explore the possibilities of char surface area contributions to the measured reaction rates, similar plots as the ones just discussed were determined using initial and 25% converted char surface areas, measured using nitrogen adsorption. The charts produced showed less normalising effect than the CO₂ surface area data discussed previously.

6 Discussion

It is generally accepted that increased pressures produce lower volatile yields, and that increased heating rates produce higher volatile yields. This work has set out to provide methods to measure VY under appropriate high heating rates, high pressure conditions and to provide a database of VY and char reactivity for the CRC coal sample suite.

It is apparent that there is a rank relationship between the effects of increasing pressure and the resultant volatile yields at high heating rates. In fact, at the pressure reported in this work, it has been shown that lower rank subbituminous coals can produce VY values higher than reported VM values at 1 atm. The semi-anthracite (281) produces significantly lower VY than VM values at 1 atm. Therefore, the WMR reactor produces volatile yields that more truly reflect the practical environments of high temperature, high pressure systems than a standard volatile matter assay. The chars produced from these tests were also found to have chemical reaction rates the same as chars produced at the same temperature and pressure in a pressurised drop tube furnace.

These results, combined with previous data¹, indicate that the WMR described in this work is a useful tool for the characterisation of coals for use in advanced technologies. This procedure, however, was shown in this work to have some limitations at the extreme end of the VM scale. Coals such as CRC 297 which has a proximate VM content of approximately 51% (daf), could not be tested in this apparatus. It is presumed that the volume of volatile material and violence of the evolution process under these conditions resulted in mesh disintegration. It remains to be seen as to whether or not this will be the case for all high-volatile coals, or if this result was specific to this coal.

The TGA testing programme used two indices for characterising char reactivity. The first was reaction rate vs conversion profiles for all chars in different reactants. The second was a measure of both the initial reaction rate and the rate at approximately 25% conversion. Surface area data for both initial and partially converted samples were determined and utilised to calculate intrinsic reaction rates.

It was observed that the initial N₂ surface area data were orders of magnitude lower than the initial char CO₂ surface areas indicating a microporous structure within the chars tested. On conversion, the N₂ surface areas approached the CO₂ surface area values indicating the opening up of these pores during reaction. This supports the use of CO₂ surface areas to determine intrinsic reactivities of chars made at high pressures and heating rates as CO₂ is seen to be accessing a greater amount of the char surface area (both before and on conversion) that is able to participate in the gasification reactions than the BET N₂ surface area measurement reflects.

The conversion profiles of the chars reacting in the different reactants showed uniquely shaped profiles for each reactant. These variations indicate differences in the development of the char structure in each reactant. This is consistent with previous surface area data obtained at atmospheric pressure²⁰,²¹ and some recent preliminary data obtained at increased pressures have highlighted this issue as one worthy of future research²².

The CO₂ intrinsic data produce for both the initial and partially reacted samples shows some normalising effects on the overall reaction rates for these chars, but, as for all samples tested here (to a greater or lesser extent) there are still other factors such as crystallinity, different maceral concentrates exposed during the conversion process etc that can also have a direct impact on reaction rates at any point in a char's conversion profile. This is particularly relevant for these chars reacting in H₂O and O₂, where the inter-char variations were largely unaffected by removing any possible effects of surface area. It was noticed that the chars with the least noticeable effect of surface area were usually the lowest-ranked chars – this is consistent with the large amount of literature suggesting that low-ranked chars have reactivities more influenced by the catalytic effects of mineral matter than the effects of a larger surface area.

7 Conclusions

Notwithstanding the enhancing effect of an increase in heating rate on a coal's volatile yield, this work shows that the volatile yields of all coals tested, other than the lowest rank sample, are suppressed at increased pressure. The greatest reduction in these yields was experienced by the highest rank coal, with the lower ranked coals showing less of an effect – although it is expected that with further increases in pressure these samples too will show a reduced volatile yield at pressure. The WMR analyses of all CRC coals demonstrates the shortcomings of using only the proximate VM value to define a coal's VY under practical high pressure conditions.

Chemical reaction rates to CO₂ presented in this report showed the greatest rank related trends of the three reactants, and also the largest contribution of char surface area to the measured (or apparent) rates. The H₂O data showed less of a coal rank trend on reaction rates and less of a contribution of surface area. The O₂ data showed the least effect of surface area on the measured rates. Furthermore, the conversion profiles of the chars in each reactant differed, suggesting a different development of the char in each gas. These data suggest that other issues such as crystallinity, mineral matter etc. are playing a greater role under these conditions and that, overall, the evolution of the char surface area is predicated by the reactant gas.

These data are of the form that allows them to be used as both inputs for gasification and combustion process models used to predict coal performance in practical high-pressure reaction systems, as well as a contribution to the resolution of problems associated with the use of Australian coals in international demonstration and pilot-scale facilities.

8 Appendix

CRC#	prox VM (daf)	VY (daf) at 15 atm
297	51.1	-
252	49.5	50.7
272	41.0	40.4
283	36.8	36.3
296	35.8	34.7
263	35.5	34.1
240	35.3	33.5
299	34.7	32.4
298	34.3	32.4
284	32.3	30.1
274	32.1	26.3
310	28.6	27.2
306	24.2	19.9
281	9.8	1.2

Table 8.1: Proximate volatile matter analyses and volatile yield results (on a dry ash free basis) for all chars tested, as shown in Figure 5.2.

(N.B. The Volatile Yield values (VY) presented here are average values determined from several runs of each coal sample on the WMR). The average error for the WMR test is no more than ~ 1 to 1.5%

CRC Coals	CO ₂ (900°C)				O ₂ (300°C)				H ₂ O (800°C)			
	Ra(0)	Ra(25)	Ri(0)	Ri(25)	Ra(0)	Ra(25)	Ri(0)	Ri(25)	Ra(0)	Ra(25)	Ri(0)	Ri(25)
252	7.91E-04	1.09E-03	2.38E-06	2.19E-06	1.00E-05	1.18E-05	3.01E-08	2.48E-08	4.18E-04	4.81E-04	1.26E-06	9.85E-07
299	4.77E-04	6.39E-04	1.50E-06	1.31E-06	1.25E-05	1.80E-05	3.94E-08	6.56E-08	7.56E-04	9.72E-04	2.38E-06	2.12E-06
272	2.12E-04	3.29E-04	9.46E-07	7.17E-07	3.80E-06	7.50E-06	1.70E-08	1.27E-08	3.76E-04	4.78E-04	1.68E-06	1.28E-06
283	1.77E-04	2.88E-04	8.18E-07	8.39E-07	3.80E-06	4.00E-06	1.46E-08	1.19E-08	2.27E-04	3.24E-04	1.05E-06	7.55E-07
263	1.79E-04	3.00E-04	8.61E-07	6.92E-07	1.83E-06	5.17E-06	8.80E-09	1.12E-08	2.52E-04	5.59E-04	1.21E-06	1.24E-06
240	1.41E-04	2.91E-04	7.92E-07	8.36E-07	5.30E-06	7.20E-06	2.98E-08	2.65E-08	2.76E-04	3.29E-04	8.52E-07	9.53E-07
296	2.33E-04	3.48E-04	9.32E-07	6.56E-07	2.50E-06	4.50E-06	1.00E-08	7.30E-09	2.95E-04	3.62E-04	1.18E-06	8.34E-07
298	2.27E-04	3.28E-04	8.70E-07	6.67E-07	2.53E-05	1.52E-05	9.69E-08	4.40E-08	2.98E-04	3.79E-04	1.14E-06	8.37E-07
274	2.84E-04	3.81E-04	8.77E-07	7.19E-07	1.72E-05	1.30E-05	5.31E-08	6.81E-08	6.29E-04	5.00E-04	1.94E-06	9.00E-07
284	1.46E-04	2.20E-04	9.11E-07	8.05E-08	4.17E-06	6.30E-06	2.61E-08	2.35E-08	3.00E-04	3.34E-04	1.87E-06	9.62E-07
310	2.01E-04	2.83E-04	9.19E-07	8.76E-07	1.22E-05	8.20E-06	5.58E-08	2.38E-08	8.03E-04	1.00E-03	3.66E-06	2.71E-06
306	1.76E-04	2.51E-04	8.04E-07	6.92E-08	8.20E-06	7.30E-06	3.74E-08	3.28E-08	6.24E-04	5.26E-04	2.85E-06	1.41E-06
281	1.10E-04	1.78E-04	5.02E-07	2.93E-07	1.05E-05	8.70E-06	4.79E-08	4.22E-08	3.72E-04	4.45E-04	1.70E-06	7.59E-07

Table 8.2: Reaction rate data for CRC coals as shown in Figure 5.13 to Figure 5.18 in decreasing rank order. $R_a(0)$ is initial apparent rate, $R_a(25)$ is converted apparent rate (25% conversion), $R_i(0)$ is initial intrinsic rate, and $R_i(25)$ is the converted intrinsic rate. Intrinsic rates calculated using CO₂ surface areas. Apparent rates have the units of g g⁻¹ s⁻¹ and intrinsic rates have the units g m⁻² s⁻¹.

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