CHAPTER 4

4.0 EXPERIMENTAL: CHAR GASIFICATION WITH CARBON DIOXIDE

4.1 Introduction

The experimental methodology and procedures employed to study the effects of various chemical and physical properties of the selected chars on the char-CO_2 gasification kinetics are presented in this chapter. A description of the thermal analysis equipment, specifications and experimental design and schedule are discussed. Materials and reaction gases used in the course of the experiments are also presented.

4.2 Materials Used

Materials used in this study are coal/char and reaction gases, which are carbon dioxide (CO_2) and nitrogen (N_2).

4.2.1 Coals and Subsequent Chars

The four low grade coal samples used for this investigation were selected from the coals supplied by Eskom to the Coal Research Group, North-West University, Potchefstroom Campus and originated from coalfields in the Highveld area of South Africa. The particle size of the samples as received, ranged from fine powder to as large as 5 cm.

These samples were prepared according to methods described in Section 3.3 and devolatilised following the procedure outlined in Section 3.4.1, to prepare the subsequent chars. The prepared chars have average particle diameters of 1000 μm < dp < 1120 μm. The coal and char samples were identified as: coals, or chars, B, C, C2 and D2 respectively. Characterisation of the coals and the resultant chars were presented in Chapter 3.

4.2.2 Reactant Gases

Reaction gases used for the char-CO_2 gasification reaction experiments were mixtures of CO_2 and N_2 (See Table 4.3, Section 4.5 for reaction gas composition). Afrox supplied both gaseous reagents. N_2 was used as inert diluent gas to control the concentration of CO_2, and a high flow rate of the mixed gases was used to eliminate external diffusion effects during experimentation. The specifications of the two reactant gases are summarised in Table 4.1.

Table 4.1 Specifications of gaseous reagents.

Reagent	Afrox item No.	Grade	Purity
Carbon dioxide, CO_2	40-RC	Technical	99.0%
Nitrogen, N_2	511204-SE-C	Nitrogen Baseline 5.0	> 99.999%

4.3 Reactivity Equipment: Thermogravimetry

A thermogravimetric analyser (TGA) was used to investigate the char-CO_2 gasification reactivity of the respective char samples. Dutta *et al*. (1977); Mühlen *et al*. (1985); Matsui *et al*. (1987); Mühlen and Sulimma (1987); Kajitani *et al*. (2006); Kaitano (2007); and Everson *et al*. (2006 and 2008a), to mention a few investigators, have successfully used TGAs in the study of gas-solid reaction kinetics. A detailed discussion on thermogravimetry was presented in Section 2.7.1.

4.3.1 Thermax 500 Thermogravimetric Analyser (TGA)

A Thermax 500 TGA supplied by Thermo Fischer Scientific, Karlsruhe, Germany was used. The TGA system is illustrated schematically in Figure 4.1 and a photograph of the system is given in Figure 4.2. Like other TGAs, it measures weight change of a sample over a given temperature and pressure range under specified environmental conditions. The specifications of the TGA are presented in Table 4.2.

The sample is loaded into a miniature platinum gauze basket, which is connected to and suspended from a sapphire extension rod or hang-down after opening the joint coupling, joining the furnace vessel and the pressure balance. The controlled temperature zone of the furnace is 50 mm. Furnace temperature follows a temperature profile sequence established by the user in a method in the Thermax software. The software periodically records time, weight, temperature and pressure according to user-defined sequence to a file on the computer and allows the user to perform analytical functions on the experimental data as well as to save to other formats that can be processed on other applications for various uses.

The Thermax 500 TGA is composed of three main parts: the mainframe; the console; and the pressure and flow controllers. The mainframe holds the equipment's hardware, including the pressure balance; the furnace vessel; the stand; and the elevator in place as shown in Figure 4.2. The console houses the equipment electronics; displays data and warnings; and connects the facility to the computer. The pressure and flow controllers control pressure in the instrument; flow rates for the

three different gas channels; indicates pressure in the instrument; and connect to the computer via an RS 232 serial transmission cable.

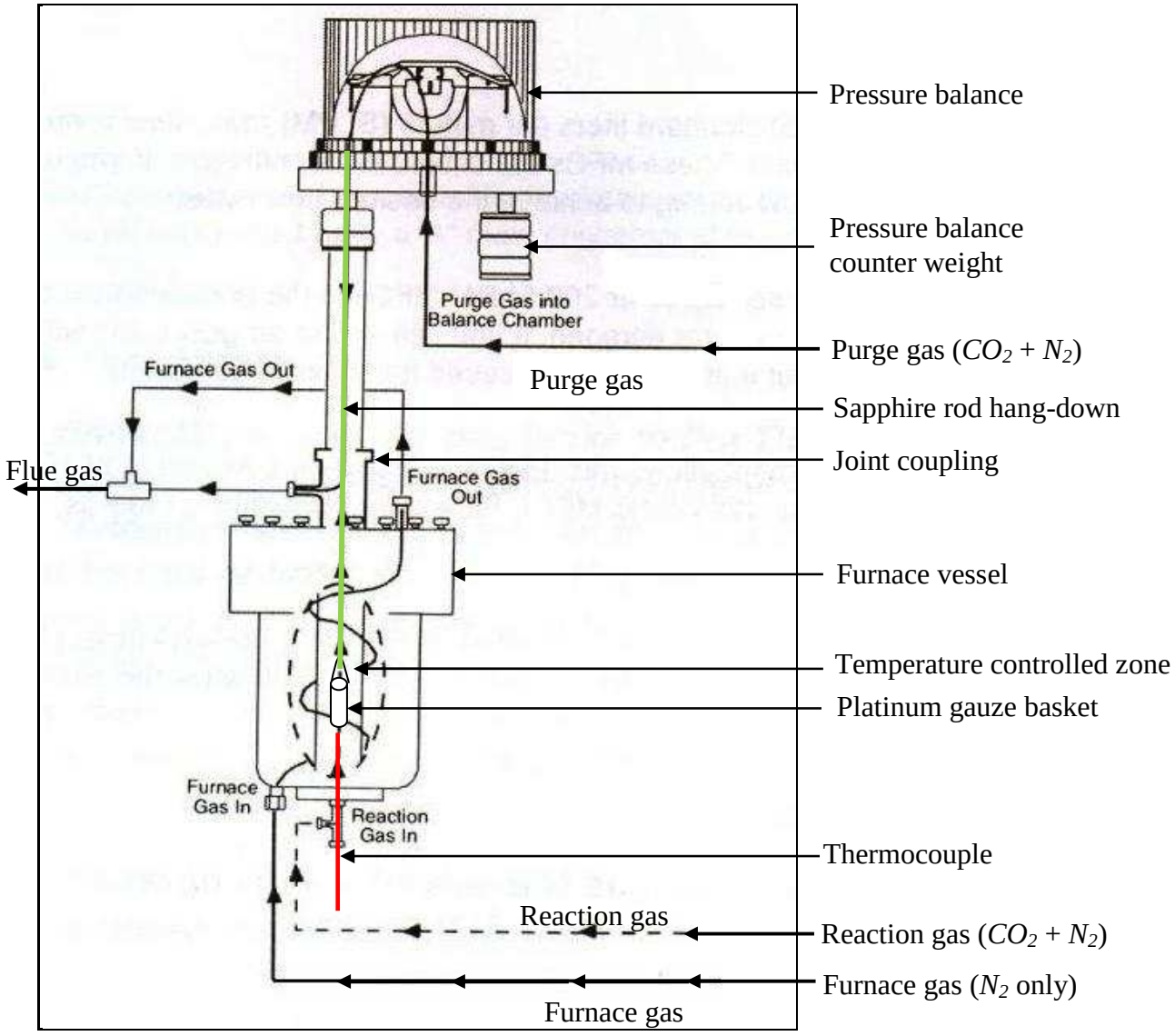

Figure 4.1: Schematic representation of Thermax 500 TGA showing the essential parts and gas flow system (Not drawn to scale).

The Pressure Balance: The microbalance used by Thermax 500 TGA is a pressurised balance consisting of two parts: a D-101 balance and a pressure head with a capacity of 100 g and sensitivity of 1 μg. However, the constraints of high pressure will usually limit the effective sensitivity to about 100 μg. Specifications of the pressure balance are given in Table 4.2. The balance also has a closed loop servo network, which

automatically compensates for weight changes in the sample. The electrical current necessary to return the balance beam to its null position is directly proportional to weight. Since this is a null balance, the sample always remains in a uniform temperature zone.

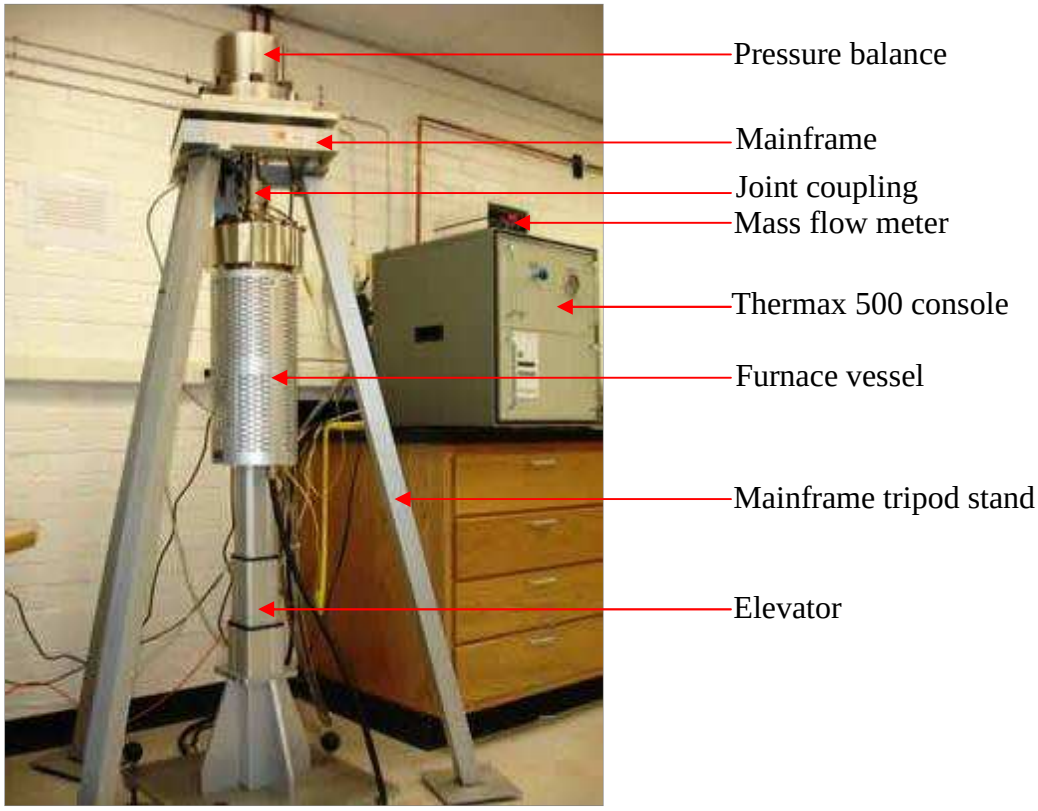

Figure 4.2: Photograph of Thermax 500 TGA showing the essential parts.

The Furnace Vessel: The furnace vessel, which was machined from solid 316 stainless steel, was constructed and inspected according to the American Society of Mechanical Engineers (A.S.M E) boiler and pressure vessel Code with the acceptance stamp on the side of the bottom plate. Black anodised spacers minimize dead volume in the balance chamber to approximately 150 cm^3. Specifications of the furnace are presented in Table 4.2. An internal quartz tube, sealed at both ends with *O*-rings, separates the reaction chamber from the furnace and prevents reactive gases from entering the furnace. A joint coupling ring was used to seal the furnace vessel to the pressure balance. The sample is loaded and unloaded when the joint is opened and the

furnace is lowered using the elevator. A cooling fan that is suspended from the balance isolates the microbalance from the heat generated by the furnace. This fan assures a stable reading from the balance. The fan is computer controlled by the Thermax software, but a fan switch on the console allows for manual control as well.

Table 4.2: Thermax 500 TGA specifications.

Pressure Balance	
Maximum load	100 *g*
Weighing range	± 10 *g*
Sensitivity	1 μg
Temperature drift	10 $\mu g \cdot ^{\circ}C^{-1}$
Accuracy at ambient temperature	>99.98 %
Repeatability	>99.999 %
Full range zeroing	Yes
Furnace	
Temperature range	
At ambient pressure	Up to 1100 *°C*
At 69 up to 100 bar	Up to 1000 *°C*
Maximum ramp	25 $^{\circ}C \cdot min^{-1}$
Thermocouple	K- type (1/8" Chromel-Alumel)
Temperature repeatability	± 3 *°C*
Pressure Level	
Maximum pressure at ambient	100 *bar*
Maximum pressure at 1000 *°C*	69 *bar*
Vacuum	5 x 10^{-4} *torr*
Reaction chamber	
Sample Volume	35 cm^3
Reactor tube volume	300 cm^3
Controlled temperature zone	50 *mm*
Oxygen free environment	Yes
Atmospheres	O_2, H_2, CO, CO_2, H_2S, SO_2, H_2O

The Thermax software (according to an established temperature profile) controls the temperature of the furnace. A standard type-*K* thermocouple, located close to the sample, detects and conveys the current temperature to the computer as well as the console. The furnace allows a temperature profile of ramps and isotherms, established by the user under constant computer control. The ramps are adjustable from 0.1 $°C \cdot min^{-1}$ up to 25 $°C \cdot min^{-1}$ depending on the user's intention.

The Stand and Elevator: The stand is a rigid tripod support with a plate and leveling screws for aligning the pressure balance. The legs of the tripod must make firm contact with the floor and resist tilting and shifting. In cases where there is extensive vibration (up to 17 Hz), a rubber mat or other isolation system may be required so that the pressure balance is not affected. The elevator allows easy raising and lowering of the furnace vessel and is controlled by a hand release system. Manual control is sometimes required to align the components. Wheels on the elevator allow the unit to be moved, but it is recommended that the lift be fixed using the adjustable feet to align the lift mechanism with the pressure balance.

4.3.2 Gas Supply

The reaction gas mixture (CO_2 and N_2) premixed in various concentrations as required for the experiment was supplied to the furnace vessel's reactor section by means of interconnected stainless steel piping. The flow rate of the furnace gas was controlled by the furnace gas mass flow controller in the TGA console, while that of the purge and reaction gases were controlled with a control unit connected to two Brooks-5850 mass flow controllers (for mixing) before connecting to the appropriate gas channel of the TGA console. Furnace gas was N_2 only, while the same gas mixture was used for both the purge gas and the reaction gas.

4.3.3 Data Acquisition Interface

A computer is required to operate the Thermax 500 TGA with the Thermax software. The test criteria, established by the user in the software are displayed on the monitor, allowing the user to fully consider them before starting the experiment. The data

acquired during the experiment (mass, current temperature and pressure) is shown on the computer display in real time and stored in computer files, which can be exported to external storage devices for further processing.

4.4 Experimental Procedure

50 ± 1 *mg* of sample (1000 $\mu m < d_p <$ 1120 μm) was used for each experiment on the TGA. An N_2 gas flow rate of 750 $ml \cdot min^{-1}$ was used for the furnace gas, while the purge gas and reaction gas composed of CO_2 and N_2 in the required concentrations were also supplied to the TGA at 750 $ml \cdot min^{-1}$. This was done to eliminate any dilution effect on the reaction gas composition that may arise if N_2 only was used for the purge gas. Furthermore, CO_2 does not have significant corrosive side effects and thus was not feared to affect the pressure balance mechanism and electronics.

Procedures for the experiments are as follows:

- All the required settings on the TGA: the initial dynamic ramp that was 25 $°C \cdot min^{-1}$ for all the experiments; the final isothermal temperature (900 - 950 *°C*); and the expected duration of the experiment (50 hours (180,000 seconds)) were set. The pressure mode was set off and TGA mode put on, as all the experiments were done at ambient pressure (0.875 *bar* in Potchefstroom). The joint coupling on the TGA was opened and the furnace vessel lowered using the manual leverage control. The empty platinum gauze sample basket was cleaned of any particles using compressed air, and then hung on the sapphire rod sample hang-down, and the pressure balance was tared from the Thermax software on the computer.

- 50 ± 1 *mg* of char sample was weighed on the Mettler Toledo AB204-S top loading balance with 0.001 *mg* sensitivity. The sample basket was removed gently from the hang-down, the weighed char sample was then loaded and hung back on the sapphire rod holder. The pressure balance was cross checked for any misalignment. If any was observed, the alignment knob was be used to correct it. If not, the furnace vessel was raised to touch the pressure balance and the joint

coupling put back and tightened with six hexagonal bolts. Sample mass displayed on the TGA console is supposed to be the same as that obtained from the Mettler Toledo balance. If this was not the case, the process was restarted.

- The TGA furnace was degassed by flushing with N_2 gas for 15 minutes on the three different gas channels. After this, the Thermax software was used to start the experiment after entering a run identificator label. The data logging programme controls the TGA in line with the preset ramp, isotherm and run duration. Traces of volatiles and or moisture (probably adsorbed by the char during and or between storage and usage) may be observed during the ramp and initial isothermal period. The TGA usually ramps to the isothermal temperatures (900, 917, 933 and 950 $^{\circ}C$) in 35 to 37 minutes. The char was left for an extra 23 to 25 minutes (one hour in total) at the stipulated isothermal temperature to make sure that there was no observable mass loss due to any volatiles or moisture.

- After confirming the constant mass of the char at the required isothermal temperature, the reaction gas (CO_2 + N_2 or CO_2 only for 100 % CO_2 experiments) was switched over manually. The purge gas, which is of the same composition as the reaction gas was switched over as required. The reaction was allowed to proceed until there was no apparent change in mass of the reacting char sample; an indication that all the "reactive" carbon and carbon compounds in the char are fully reacted and that the unreacting or "uncombustible" residue corresponds to the ash with some "unreactive" highly aromatic carbons.

4.5 TGA Experimental Programme

Experiments were planned to include two different variables: isothermal reaction temperature and CO_2 concentration in the reaction gas mixture, and four different char samples were used. The experimental data from the TGA Thermax software were evaluated in detail to determine the kinetics of the gasification reaction as well as the contribution(s) of the various char properties to the overall reaction. These results were used to deduce a suitable kinetic model to fit the experimental data. The outline

of experimental design followed in this investigation is given in Table 4.3. It should be noted that all experiments were conducted at ambient pressure (0.875 *bar*).

Table 4.3: Reaction conditions for char-CO_2 gasification experiments.

Variable	Ranges and compositions
Reaction	Gasification of char with CO_2
Char samples	B, C, C2 and D2
Char production temperature (in PBBR)	900 *℃*
Char sample mass	50 ± 1 *mg*
Char particle diameter	$1000 < d_p < 1120$ μm
Initial ramp (N_2 atmosphere)	25 $℃ \cdot min^{-1}$
Isothermal reaction temperatures	900, 917, 933 and 950 *℃*
Reaction gas flow rate	750 $ml \cdot min^{-1}$
Reaction gas mixture (CO_2+N_2)	25, 50, 75 and 100 % CO_2
Reaction Pressure	Ambient (0.875 *bar*)
Number of Experiments without reproducibility	64 *experiments*