

## CHAPTER III

### EXPERIMENTAL SECTION

#### 3.1 Materials

Two graphites (SP-1 and Micro 450 graphite) were used in this study. The SP-1 graphite was obtained from Union Carbide and the Micro 450 graphite was from Asbury Graphite Mills. Both samples were highly graphitic, of high purities and were of uniform disk-shaped sizes.

Table 3.1 Properties of two graphite samples used (Yang and Chen, 1993)

Sample	BET (m <sup>2</sup> /g)	d (μm)	h (μm)	A <sub>1</sub> (m <sup>2</sup> /g)	A <sub>2</sub> (m <sup>2</sup> /g)
SP-1	2.01	33	0.46	1.95	0.054
Micro 450	18.90	2.05	0.05	18.01	0.89

Notes:  $d$  = average diameter of the graphite flakes.

$h$  = average thickness of the graphite flakes.

$A_1, A_2$  = basal plane and edge plane surface areas, respectively

Nitric oxide gas used was in a purity of 99.5% and was supplied by Intergas Co. Ltd.. Helium used as diluent and carrier gas for GC was in a minimum purity of 99.999% and obtained from Thai Industrial Gases Public Co., Ltd.

## 3.2 Experimental Apparatus

The apparatus for studying the gasification rate of graphite with NO is shown schematically in Figure 3.1. The system consists of 3 parts: gas blending system, TGA reactor, and analytical instrumentation.

### 3.2.1 Gas Blending Systems

Nitric oxide and helium were supplied from cylinders. The regulators were installed to the cylinder valves to control the delivery pressure of gases. The regulator used with nitric oxide was a two-stage stainless-steel regulator with CGA 330 connection. A brass regulator with CGA 580 connection was used with helium. The working pressure of both gases in this work were set at 30 psia. For helium, an indicating moisture trap and an oxygen trap were used inline to remove impurities such as H<sub>2</sub>O and O<sub>2</sub> in order to prevent side reactions.

There were two streams in the line; pure nitric oxide and helium. Each of feed streams was first passed through a NUPRO 7 micron filter to remove contaminants. Then the flow rate of each gases were controlled by Side-Trak Model 840 mass flow controllers. This mass flow controllers will give the outlet pressure at 1 atm if the pressure input is in the range of 20-30 psia. Therefore the reaction was carried out at atmospheric pressure. To control unidirectional flow, NUPRO check valves were installed inline also. Each feed stream was mixed and then the NO concentration was checked by passing to Gas-Chromatography before fed to the TGA reactor.

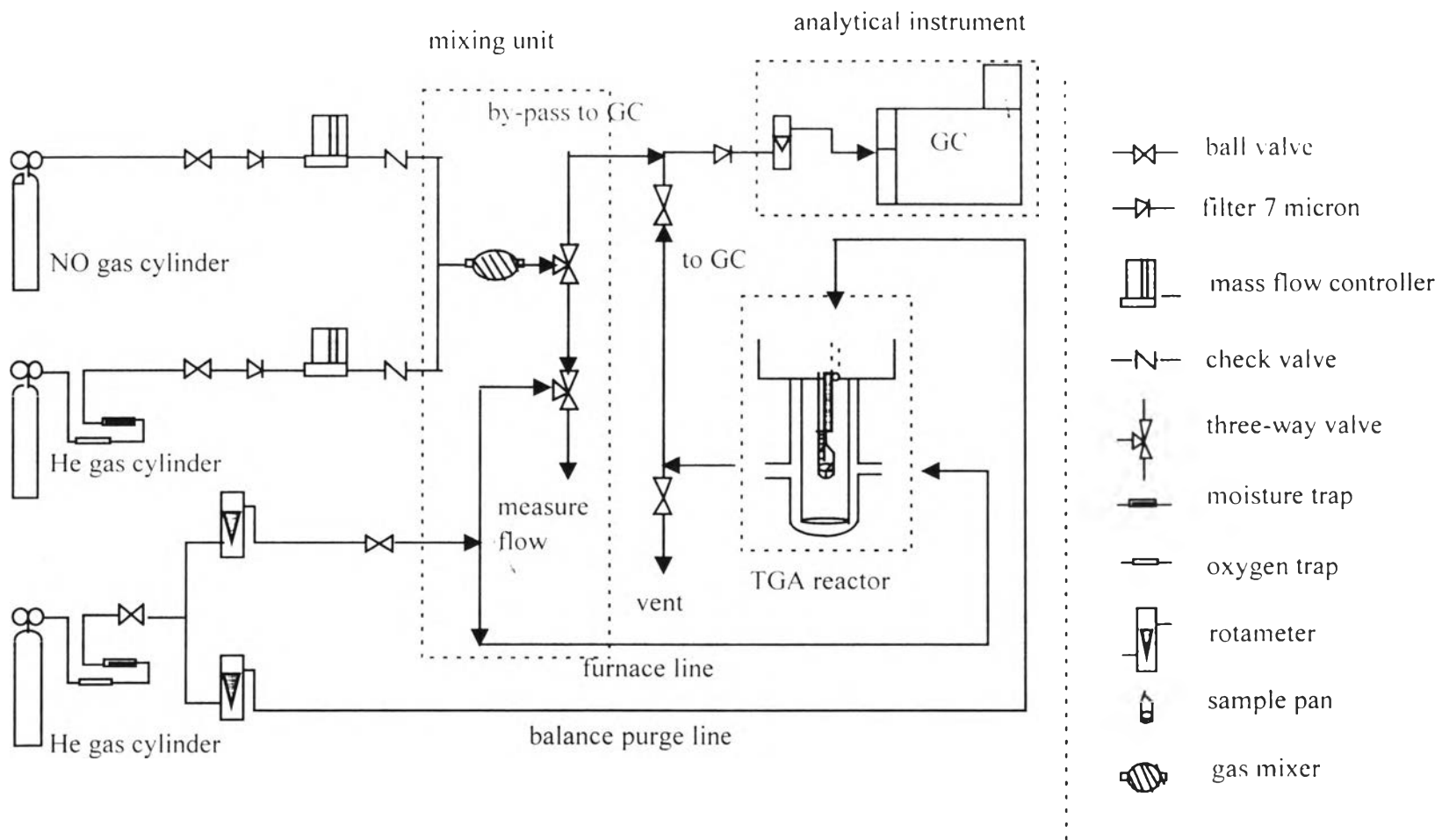


Figure 3.1 The schematic diagram of the experimental apparatus used.

### 3.2.2 TGA Reactor

The apparatus used for measuring graphite gasification rates with nitric oxide was a Du Pont thermogravimetric analyzer (TGA) by Du Pont, model TGA 2950 for which its sensitivity was 0.1  $\mu\text{g}$ . It measured the amount and rate of weight change in graphite when reaction occurred. Three main components in the TGA reactor used should be mentioned in the following.

*3.2.2.1 Gas Lines to TGA Reactor.* There were two lines going to the TGA reactor. First was the balance purge line which flowed vertically from the balance chamber to the furnace. To prevent gas products from contaminating the sensitive balance mechanism and to prevent corrosion of the balance, an inert gas must be used in this balance line. The balance purge maintained a positive pressure in the balance chamber so back diffusion of gases from the furnace to the balance chamber was prohibited. Second was the furnace line. Nitric oxide was passed through this line to react with graphite in the sample pan

The flow rate of gas going to this reactor must be less than 100 ml/min because of sensitive balance. Moreover it was important to maintain the proper ratio of flow rates between the balance chamber and the furnace housing. A flow distribution of 40 percent to the balance chamber and 60 percent to the furnace was recommended. In this work, helium which used in balance line was set at the flow rate of 40 ml/min. While the reactant gas, nitric oxide, was set at 60 ml/min, the total flow rate was 100 ml/min.

*3.2.2.2 Thermocouple.* Heating rate and sample temperature were measured by Platinel II thermocouple located above the sample.

*3.2.2.3 Sample pan.* The sample pan used is 100  $\mu\text{l}$  size alumina ceramic ( $\text{Al}_2\text{O}_3$ ) with 0.4 inch diameter.

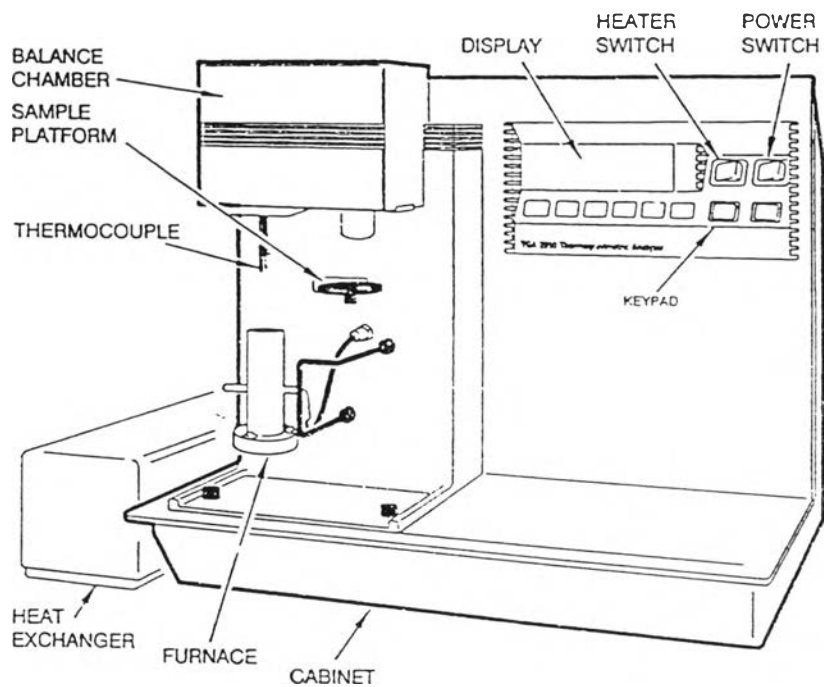


Figure 3.2 The parts of the TGA 2950 Module (Du Pont Company, 1990).

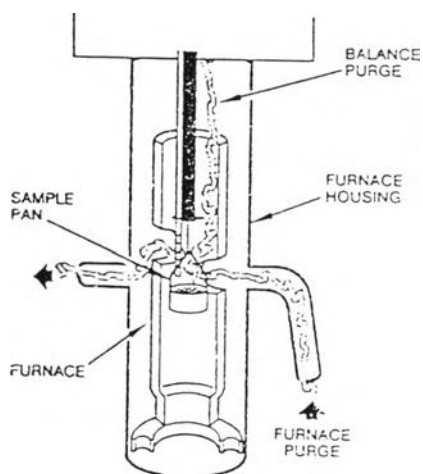


Figure 3.3 The furnace purge (Du Pont Company, 1990).

### 3.2.3 Analytical Instrumentation

The effluent gas leaving the reactor was analyzed using a Hewlett Packard 5890 SII and Fison (8000 series) Gas Chromatographs equipped with a thermal conductivity detector (TCD). Helium was used as a carrier gas at a flow rate of 25 ml/min. GC's were used and the analytical conditions were as follows:

1. For N<sub>2</sub> and NO detection, a molecular sieve 13X column was employed at 30 °C.
2. For CO<sub>2</sub>, a Porapak Q column was operated at 55 °C.

The weight of graphite was monitored by TGA and also the rate of weight changed in graphite was measured when the reaction occurred.

### 3.3 Procedures

In a typical kinetic experiment, the graphite gasification with nitric oxide were carried out in the TGA reactor as described previously. The graphite samples were weighed to an accuracy of 5 mg and then deposited into the sample pan. Then it was degassed at 120 °C in helium for 2 hours in order to remove the physically adsorbed gases. Helium with flow rate of 40 and 60 ml/min was used in balance line and furnace line respectively in this degassing step. After degassing, the reactor was brought to the desired temperature with the rate of 10 °C/min under an atmosphere of pure helium. Then the helium in furnace line was changed to the reaction gas mixture.

Nitric oxide and helium was mixed at desired concentration and its concentration was checked by GC. When the desired temperature was reached, 60 ml/min of a nitric oxide/helium mixture was then introduced to the reactor

by furnace line and the reaction took place. The gaseous reaction products were intermittently withdrawn from the reactor and was further analyzed by GC.

### **3.4 Kinetic studies**

The rate per active site, turnover frequency (TOF), of the gasification of graphite with nitric oxide (6%, 20% and 40%) was determined at a total pressure of 1 atm and in the temperature range of 500-800 °C. To determine the activation energy and the temperature "break" in Arrhenius plots of this carbon-nitric oxide reaction, the reaction was carried out at the temperature between 500-800 °C. The dependency of the concentration of nitric oxide reacted on temperature "break" in Arrhenius plots was also studied in the same range of temperature by varying the NO concentration.

#### 3.4.1 TOF as a Function of NO Concentrations.

To study the influence of partial pressure of NO concentration; the NO partial pressure was varied between the se sample were used. The total volumetric flow rate was kept at approximately 100 ml/min and the total system pressure was maintained at atmospheric pressure. Temperatures investigated were between 500-800 °C. The TOF rates of graphite gasification with NO were determined as a function of NO concentration.

#### 3.4.2 TOF as a Function of Reaction Temperature

All experiments were conducted by feeding NO at a flow rate of 100 ml/min to the reactor contained 5 mg of graphite sample under atmospheric pressure. The temperature was varied from 500 to 800 °C and the NO concentration investigated were 6%, 20% and 40%.

Table 3.2 Experimental conditions for this study

wt. of graphite	5 mg.
gasification temperature	500-800 °C (the increment of 50 °C )
NO concentration in helium	6%, 20%, 40%
flowrate	100 ml/min
heating rate	10 °C/min
total pressure	1 atm