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An Introduction of an Apparatus for Rapid Heating Coal Gasification

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Cahn Balance를 이용한 급속 가열방식의 석탄가스화 장치 소개

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Abstract : An experimental reactor system was devised and employed to examine catalytic coal gasification. A 4-kw tungsten halogen lamp heater combined with a graphite sample basket coated with silicon nitride film made rapid heating and cooling possible. Also a small graphite cap on the thermocouple tip which located just beneath the sample basket helped remarkably to read real temperatures. Silicon nitride film on the basket and the cap showed very good protection against the reaction between graphite and oxidant gases during the experiments. The weight of specimen could be continuously measured without disturbance.
(Key words : coal gasification apparatus : rapid heating : graphite : protective film)

요 약

실제 실험 시간에 따른 시료의 무게변화와 생성가스의 조성 측정을 동시에 진행할 수 있는 실험실 규모의 장치를 칸 발란스를 이용하여 제작하였다. 급속 가열이 가능하도록 텅스텐 할로겐 등을 이용한 복사가열 방식을 채택하였고 시료 접시는 복사열을 충분히 흡수하도록 흑연을 사용하였다. 석탄가스화 실험조건에서 이 흑연이 반응기체와 반응하는 것을 막기위하여 실리콘나이트라이드로 코팅하였고, 시료 접시 바로 밑에 위치한 열전쌍에도 같은 방식으로 제작된 흑연 모자를 씌워 복사열 흡수능력이 서로 다른 흑연(시료 접시)과 금속체(열전쌍) 사이에서 생길 수 있는 온도 측정의 오차를 최소화 하도록 하였다. 이 장치를 사용한 결과 상온에서 섭씨 800도까지 3분 이내에 온도상승이 가능하였으며 시료 접시의 무게변화없이 실험중 석탄 시료의 무게 변화와 가스 조성을 동시에 측정할 수 있었다.

1. INTRODUCTION

Coal gasification has been widely investigated since 19 th century. Therefore, many kinds of experimental apparatuses have been devised to more precisely understand the phenomena occurring during coal gasification reaction. Although most of them possess some uniqueness in design in order to get more informations about the reaction, they may be classified into two types : packed bed type[1,2,3] and thermobalance type[4,5,6].

The packed bed type which is the simpler of the two in appearance and preparation, usually has an advantage over the other in setting-up and managing the reaction system. But it inherently tends to suffer from the lack of freedom of controlling the heating rate. A very rapid heating is almost out of reach with this type. It is well-known that heating rate is one of the major parameters to govern devolatilization step, char properties and eventually the whole gasification process. For the packed bed system, nothing but gas product analysis available as a probing tool during an experiment, which takes considerable time to get, usually raises another problem of difficulty in continuous monitoring of the reaction and mass balance.

Hence, when rapid heating and continuous monitoring is needed, the thermobalance type becomes more practical to choose. A typical thermobalance reactor system consists of three parts : a preheated zone where predetermined temperature is maintained, a sample basket suspended by a wire which is connected to highly sensitive weight transducer and subsquently to a recording device. Rapid heating can be achieved by dropping the sample basket to the preheated zone from the position above and continuous change of sample weight can be monitored throughout the experiment. This configuration, however, has its own flaws, too. While lowering the sample basket, sample might be spilled over without extreme precaution. Moreover, at the first stage of the reaction, the vibration of suspension wire resulted from the lowering motion of sample basket hinders a precise measurement of sample weight change.

Considering these flaws of conventional reactor systems, a new reactor design should meet the following requirements in order to obtain more correct data ;

1) Rapid heating as well as slow heating has to be achieved without any difficulties.

2) Continuous monitoring of sample weight with stability at initial stage of the reaction must be guaranteed.

3) Deviation of measured temperature from the real temperature should be minimum, say $\pm$ 2 °C.

The objective of the present study is to propose a suitable experimental apparatus which satisfies the above requirements.

2. EXPERIMENTAL

A Cahn balance (Model : Cahn 2000) equipped with a quad-elliptical radiant heater (four 1-kw tungsten halogen lamps) was employed to carry out the coal gasification experiments. Figure 1 shows the schematic diagram of the system. It was expected that radiant heating method would be more efficient for rapid heating than conventional resistant heating. In conjunction with the heater, sample basket was made of graphite, a black body, for maximum absorption of infrared rays. In this case, it is quite necessary to prevent graphite from reacting with oxidant gases under gasification condition while sustaining black color. The protective and translucent silicon nitride film was coated on the graphite sample basket by plasma enhanced chemical vapor deposition (PECVD) method. The details of the deposition condition are listed in Table

Table 1. Deposition Condition of Silicon Nitride

Parameter	Value
R. F. Power	50 W
Pressure	0.3 torr
Substrate temp.	300 °C
$SiH_4/NH_3/H_2$ mole ratio	6/15/100
Electrode space	4 cm

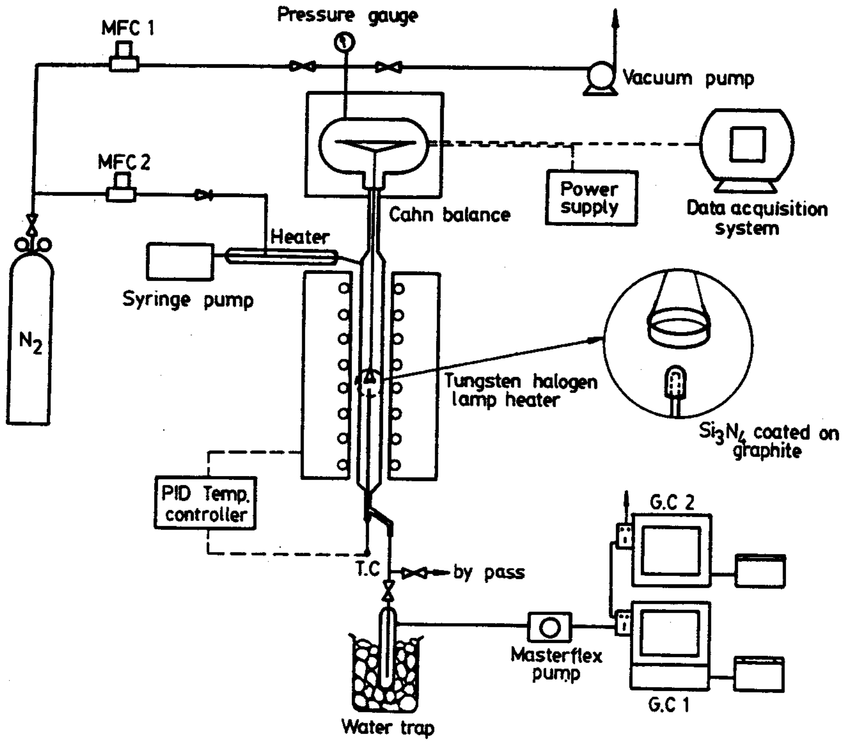

Fig. 1. Schematic diagram of the experimental apparatus.

1. Deposition of protective film on the basket was carried out in a cylindrical prasma reactor (39 cm ID× 27 cm H). After deposition, the basket was annealed at 800 °C for an hour under nitrogen atmosphere.

To evaluate the performance of the appatatus, a sample of coal with or without catalyst was put into the basket positioned at the center of the heater. Then the reactor was evacuated and purged with nitrogen alternately for three times at room temperature. After oxygen was completly removed from the reactor, the heater was turned on. On reaching a predetermined temperature, reactant gases were introduced to the system. In the course of reaction, the weight change of sample was recorded continuously and the exit gases were analyzed by a couple of gas chromatographys.

3. RESULTS AND DISCUSSION

3. 1. Stability of the sample basket under gasification condition

The physical and chemical stability of sample basket during an experiment is of great importance. A graphite sample basket is very good for absorption of infrared rays in comparison with a platinum basket which is commonly used in Cahn balance. But it has critical disadvantage of being easily degraded to CO or CO_2 under the gasification conditions. This is why silicon nitride film was coated on the basket. It was expected that the film would provide excellent protection against the reaction between graphite and oxidant gases without color change.

Figure 2 shows the result. As expected, at 750 °C and 800 °C under N_2 and H_2O atmosphere, weight

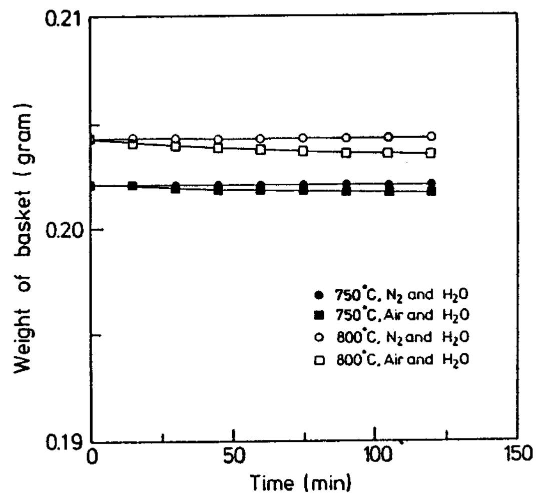

Fig. 2. Weight change of sample basket coated with Si_3N_4 under gasification condition.

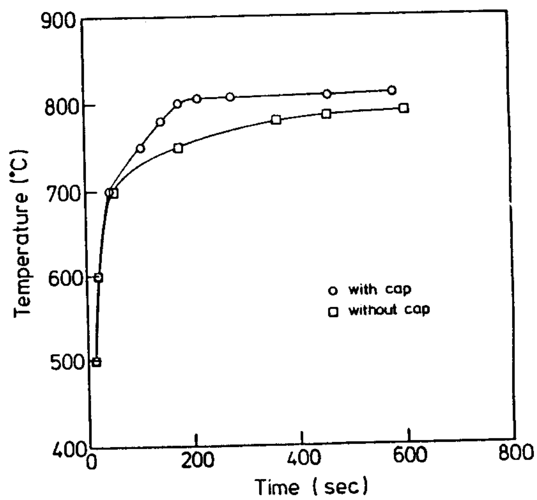

Fig. 3. Performance of radiation heater. (4 kw, set temp. : 800 °C)

loss of graphite sample basket was virtually negligible at least for 2 hours. However, under O_2 and H_2O atmosphere weight of the basket slightly decreased with time possibly due to the oxidation reaction. Imperfection of silicon nitride film on graphite, for example cracks or pin holes, probably caused diffusion of oxygen through the silicon nitride film and consequently gasification of graphite. Even though only two sets of data were collected, the reaction seemed to be limited by O_2 diffusion step through the holes rather than by surface reaction. Otherwise, weight loss would be much larger at 800 °C. This problem can be solved by either mutiple deposition method or employing longer deposition time. In this study, none of them was tried because 0.2 % of weight loss (0.4 mg) is acceptable in terms of experimental error.

3. 2. Temperature reading and heating rate

A K-type thermocouple located just beneath the sample basket and a PID controller were uses to read and control the temperature. The sample basket was heated by 4-kw radiant heater. As shown in Figure 3, it took about 200 seconds and more than 20 minutes

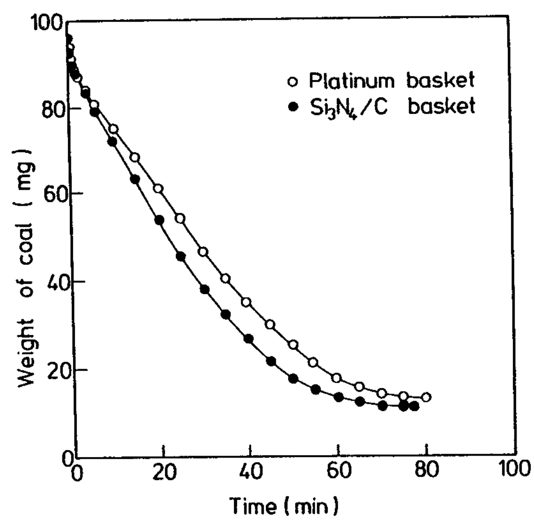

Fig. 4. Apparent gasification rates : Platinum basket vs. Graphite basket.(750 °C, N_2=60 ml/min, H_2O=1.0 g/hr, 0.08 g K/g char)

to reach 750 °C and 800 °C, respectively, when a bare thermocouple used. This is much superior to a conventional resistant heater but still dissatisfactory for rapid heating. And it is also doubtful that a bare themocouple was able to read the real temperature of the basket because shiny tip of thermocouple can not be as same as in ability to absorb radiation heat as graphite can.

As a remedy for these problems, a small graphite cap coated with silicon nitride film was capped on the tip of thermocouple. The result was quite interesting. In spite of using the same heater, as shown in Figure 3, it took only 200 seconds to reach 800 °C. What is better, it was thought to be much closer to represent real temperature of the basket. Figure 4 may confirm the above explanation. In spite of same temperature reading, the gasification rate measured with a platinum basket appeared to be slower than that with a graphite basket due to the inferior ability of platinum to graphite in absorbing radiation heat.

3. 3. Data collection

3 sets of data of the gasification experiments summerize the performance of the apparatus in Figure 5. The apparatus worked so satisfactory that initial warbling of data, which had been often observed in other thermobalance system due to the lowering motion of basket, was not detected. Considering of the fact that the sensitivity of Cahn balance was set by the unit of mg, the result was beyond expectation. The result shows that the improved apparatus with the capability of continuous monitoring of sample weight change without initial warbling in addition to the product gas analysis will give great help to illucidate the phenomena of coal gasification more precisely.

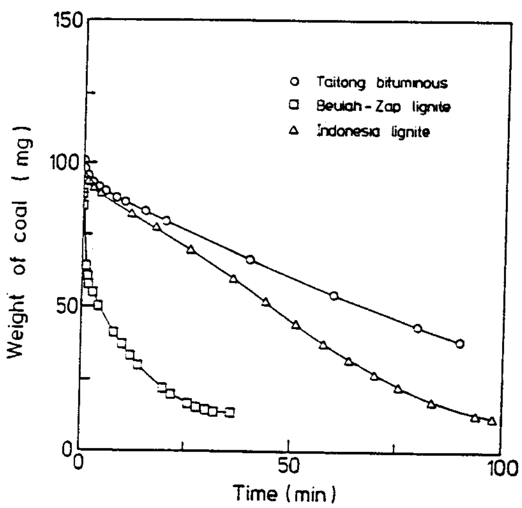

Fig. 5. Performance of the apparatus in the gasification experiments.(750 °C, N_2=60 ml/min, H_2O=1.0 g/hr, 10 wt % K_2CO_3, physical mixing)

4. CONCLUSIONS

A new experimental reactor system for coal gasification was devised and tested. Rapid heating (4 °C /sec) was easily accomplished by a 4-kw tungsten halogen lamp heater along with a graphite sample basket. Silicon nitride film on the graphite sample basket exhibited excellent protection against the reaction between graphite and oxidant gases under severe gasification condition, indicating graphite can be used for radiant heating. Also it was noticible that the small graphite cap on the thermocouple tip made temperature reading much closer to actual one. In addition, it reduced the time for thermocouple to reach the system temperature. And the design of no moving procedure during an experiment greatly helped to get rid of the initial warbling motion of sample basket which usually raised the problem in analyzing the initial stage of coal gasification reaction in conventional system.

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