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High Pressure Steam Gasification of Coal

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Synopsis

A high pressure reactor for the steam gasification of coal was constructed and tested for two Japanese coals. The gasification rate was determined as a function of temperature, steam pressure, partial pressure of hydrogen added to steam, and steam feed rate. The reactivity increased with steam pressure. Nickel salt was impregnated on coal to investigate its catalytic activity. The degree of the advantage by catalyst utilization decreased with increasing steam pressure. The size of residual char for Shin-Yubari coal was interpreted by the unreacted core model.

I. Introduction

In the previous paper⁽¹⁾, we have studied the nickel-catalyzed steam gasification of coal at an ambient pressure. The effect of catalyst and liquid ammonia pretreatment on the reactivity of coal has been demonstrated. For the practical purpose, the gasification at high pressure is desirable, since the throughput per reactor and the concentration of methane increased with gasification pressure⁽²⁾. In order to investigate the gasification behavior of coal at high pressure, we constructed a bench scale apparatus which can be pressurized with steam up to 3 MPa. By using this apparatus, we studied the gasification of two Japanese coals as a function of temperature and pressure. The effect of mixing of hydrogen with steam was determined. In several experiments, we used coals which had been pretreated with liquid ammonia and impregnated with nickel catalyst. The elemental analysis and the size analysis of residual chars also were made.

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II. Experimental

1. Coal

Table 1 shows the analyses of two coals selected for this study. Shin-Yubari coal, a caking coal, has been known to be one of the coals whose reactivities were greatly enhanced by the nickel catalyst⁽³⁾. On the other hand, Taiheiyo coal is a non-caking coal, and its reactivity could not be increased in the presence of catalyst. Some of samples were treated with liquid ammonia and impregnated with nickel salt by the method described elsewhere⁽¹⁾. Coal particle sizes ranging from 1 to 2 mm were used in all runs.

Table 1. Analysis of coal

Coal	Proximate analysis (wt%)				Ultimate analysis (wt%, daf)				
	Moisture	VM	FC	Ash	C	H	N	S	O
Shin-Yubari	1.1	38.0	55.8	5.1	86.8	5.6	1.9	0.3	5.3
Taiheiyo	5.8	46.5	36.9	10.8	77.0	6.3	1.5	0.3	14.9

2. Apparatus

Figure 1 illustrates the schematic diagram of gasification system. The reactor was 1630 mm long and was constructed from Inconel 600 tubing, 40 mm i.d. The reactor was heated by an induction heater, and it had a wide constant temperature region longitudinally. Distilled water was supplied at a constant feed rate to a vaporizer and a superheater. The superheated steam was then passed through the reactor. When the temperature, pressure and steam flow rate became

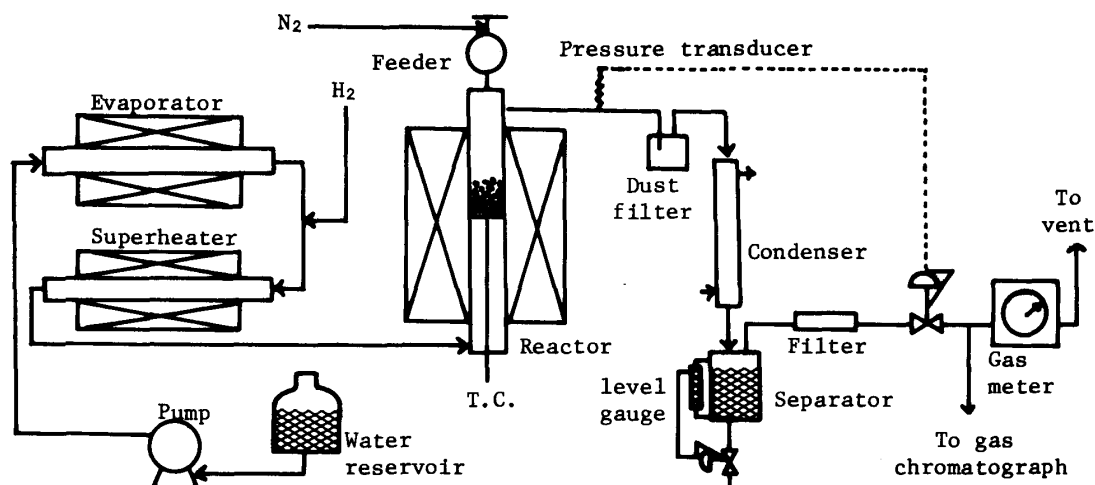


Fig. 1. Schematic diagram of gasification system.

stationary, 30 g of coal sample was charged by means of a rotary feeder at a rate of 1 g/s. The gasification was allowed to continue for 2 h. Hot gas from the reactor passed through a cooler where the unreacted steam was condensed. The product gas passed through a filter and then the pressure-reducing, back-pressure regulator, which was used to control automatically the reactor pressure. Exit gases were metered and recorded by a wet-test meter.

A small portion of this stream was passed through a gas-analyzing system which consisted of two gaschromatographs. A high speed gas-chromatograph, Yanaco HSG-1, analyzes CO_2 by a Porapak Q column, and then N_2 , CH_4 , CO by a molecular sieve 13X column. Another one, Yanaco G-1800T with an activated charcoal column, was used only for analyzing H_2 . The time required for these analyses was only 3 min. The residence time of the product gas in the system was estimated at around 1 ~ 5 min, depending on the pressure. The gas flow could be regarded as a plug flow. Thus, the results from this analyzing system would reflect quite well the gas composition in the reactor.

The secondary reactions of the product gases may take place in the gas phase or on the reactor wall. In order to check this possibility, we introduced CO gas into the reactor in the absence of coal. At the water feed rate of 1.2 kg/h, the conversion of CO to CO_2 by the shift reaction was estimated at 4%, and that by the disproportionation reaction was also 4%. They increased with a steam flow rate. Although the cracking of CH_4 also was observed, the conversion was less than 2%.

3. Presentation of data

The conversion of coal after gasification for 120 min, $X_{\text{coal}}(120)$, was calculated on a dry, ash-free basis according to Eq. 1,

$$X_{\text{coal}}(120) = 1 - \frac{R(120)}{F} \quad (1)$$

where F and $R(120)$ denote the weight of coal feed and residue at 120 min, respectively. The kinetic behavior during the period of gasification was followed only by gas analysis, and therefore the data were processed on a carbon basis. The conversion of gasifiable carbon at t min, $X_c(t)$, was defined as

$$X_c(t) = \frac{CG(t)}{CG(\infty)} \approx \frac{CG(t)}{CG(120) + CR(120)} \quad (2)$$

where $CG(t)$ means the weight of carbon in gaseous products, CH_4 , CO , and CO_2 , at t min, and $CR(120)$ denotes the carbon content in the

residual char after 120 min gasification. This value was determined by an elemental analysis of char (see III.5). It was assumed that no liquid products would be obtained after 120 min. The denominator in Eq. 2 represents the total weight of carbon which can be gasified.

III. Results and Discussion

1. Effect of reaction temperature

The total conversion of coal at around 0.4 MPa are listed in Table 2 as a function of temperature. The conversions of carbon are also shown. The total conversion of carbon was simply calculated from the amount of carbon in coal feed and CR(120). The conversion to gas was obtained from CG(120). As the difference of these two values, we obtained the carbon conversion to liquid, which was independent of the reaction temperature. Thus, the increase of the total conversion with temperature is mainly due to the increase in the gaseous products.

Table 2. Effect of gasification temperature on conversion.

Coal	Temperature (K)	Coal conversion 100 X _{coal} (120)	Carbon conversion (%)		
			Total	Gas	Liquid
Shin-Yubari*	1030	46	44	22	22
	1070	58	55	32	23
	1100	71	69	45	24
	1130	82	81	58	23
Taiheiyo**	900	74	69	37	32
	930	85	82	48	34
	970	93	91	57	34

* Pressure, 0.34 MPa; Water feed rate, 1.2 kg/h

** Pressure, 0.4 MPa; Water feed rate, 0.6 kg/h.

The kinetic data for Shin-Yubari coal are plotted in Figure 2 for an unreacted core model process, Eq. 3⁽⁴⁾.

$$\frac{d X_c(t)}{d t} = k [1 - X_c(t)]^{\frac{2}{3}} \quad (3)$$

Except for the initial rapid stage of gas evolution, straight line plots were obtained. The slope of the plot gave a value closely related to k. The apparent activation energy was estimated at around 130 kJ/mole. This value suggests that mass transfer severely limited

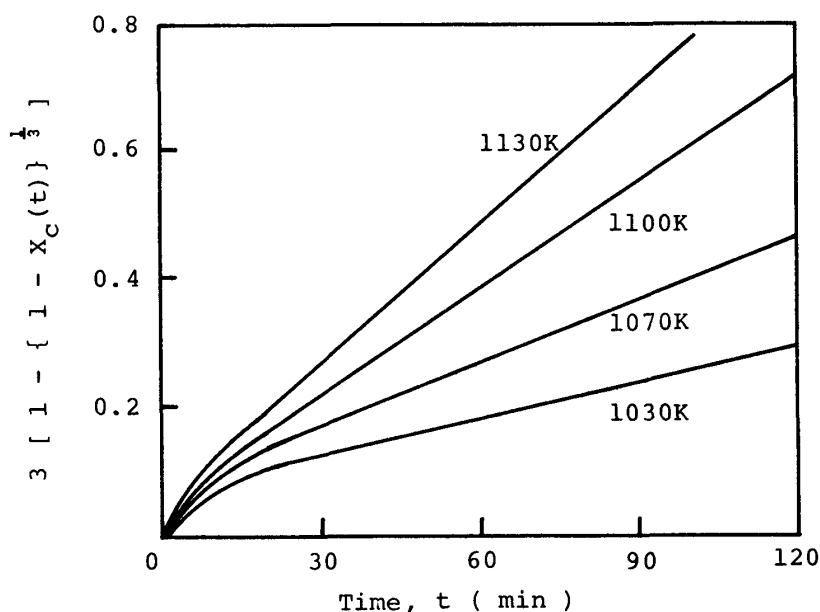


Fig. 2. Rate plots for the steam gasification of Shin-Yubari coal at 0.34 MPa.

the rate of gasification. In the case of Taiheiyo coal, the data are found to fit nicely into the first order rate expression instead of the above equation. The temperature dependence of the rate was almost the same as Shin-Yubari coal.

2. Effect of steam pressure

Table 3 summarizes the effect of steam pressure on the conversion and the composition of gaseous products in the gasification of Shin-Yubari coal. In these experiments, the water feed rate was kept constant at 1.2 kg/h. Therefore, the mean residence time of steam in the reaction zone increased with increasing steam pressure. The coal conversion increased with pressure, and this fact can be explained by assuming the well-known rate equation for the carbon-steam reaction⁽⁵⁾.

Table 3. Effect of steam pressure on conversion and gas composition*.

Pressure (MPa)	Coal conversion 100 X _{coal} (120)	Product gas composition (%)			
		H ₂	CO	CO ₂	CH ₄
0.34	58	58	13	20	9
1.0	66	58	15	18	9
2.0	73	58	17	17	8

* Coal, Shin-Yubari; Temperature, 1070K; Water feed rate, 1.2 kg/h.

$$\text{Rate} = \frac{k_1 P_{\text{H}_2\text{O}}}{1 + k_2 P_{\text{H}_2} + k_3 P_{\text{H}_2\text{O}}} \quad (4)$$

The partial pressure of hydrogen was extremely low under this experimental condition. The rate, thus, increases with increasing steam pressure.

High pressure gasification is desirable to obtain methane rich gas. However, in the present case, the product gas composition was hardly affected by pressure. Methane concentration remained almost constant. Most methane was produced in the pyrolysis stage, and little in the char gasification stage because of a high reaction temperature.

3. Effect of hydrogen

Most of the available data, including ours in the preceding section, were obtained in pure steam. However, it is necessary to take into account the effect of the primary product, hydrogen and others, on the rate of gasification, since the hydrogen concentration in a practical gasifier cannot be neglected⁽⁶⁾. The reactivity of Shin-Yubari coal with the coexistence of hydrogen was determined at a total pressure of 1 MPa. Table 4 shows that the addition of hydrogen resulted in the decrease of the rate for the steam gasification. The strong adsorption of hydrogen to the active site on the char surface might retard the reaction. The formation of carbon oxides was greatly suppressed. The decrease in the rate could be expressed fairly well in the form of Eq. 4. The relative amount of methane in the product gases increased, but the absolute value was affected little by the presence of hydrogen as shown in Table 4. Direct methane formation from carbon and hydrogen may be improbable under this relatively mild reaction condition.

Table 4. Effect of hydrogen partial pressure*.

Hydrogen pressure (MPa)	Coal conversion 100 X _{coal} (120)	Conversion of gasifiable carbon to		
		CO	CO ₂	CH ₄
0.0	58	11	16	12
0.1	51	4	8	13
0.2	45	4	6	13

* Coal, Shin-Yubari; Temperature, 1070K; Total pressure, 1.0 MPa; Water feed rate, 0.60 ~ 0.48 kg/h.

The conversion value without hydrogen, 58%, is somewhat smaller than that shown in Table 3, 66%. This apparent discrepancy is due to the different water feed rate. Generally speaking, the larger the water feed rate, the larger the reaction rate.

4. Effect of ammonia treatment and catalyst impregnation

The effect of catalyst on the steam gasification of Shin-Yubari coal which was pretreated with liquid ammonia was shown in Table 5. The comparison was made by the conversion of gasifiable carbon. The difference between the original coal and the treated coal decreased with pressure. Nickel nitrate was found to be more effective than hexaammine nickel carbonate as a starting salt material. It may be noteworthy that methane concentration at 2 MPa increased from 8% to 11% upon the addition of catalyst. The nickel catalyst was known to be more active in the methane forming reaction than in the water gas reaction⁽³⁾.

Table 5. Effect of catalyst at different steam pressure*.

Pressure (MPa)	100 X _c (120)		
	No catalyst	1% Ni(NH ₃) ₆ CO ₃	1% Ni(NO ₃) ₂
0.34	46	50	54
1.0	51	54	-
2.0	60	62	-

* Coal, Shin-Yubari; Temperature, 1070K; Water feed rate, 1.2 kg/h.

5. Characterization of residual char

Table 6 shows the ultimate analyses of various chars of different conversions. This table tells us the relative gasification rate of each element. Of course, the content of carbon increased as the gasification proceeded. However, a considerable amount of other elements still remains in char even at a high conversion. It can be safely said that, after the devolatilization stage, the elemental composition hardly change with further gasification. The variation of oxygen content is particularly interesting. Taiheiyo coal contains a substantial amount of hydroxy and carboxyl groups as oxygen containing functional groups⁽⁷⁾, and these might be quickly released upon the devolatilization as implied in Table 6. On the other hand, Shin-Yubari coal has only small amount of oxygen containing groups, and therefore the change upon the devolatilization might be small. The reaction intermediate during the steam gasification must consist of

Table 6. Ultimate analysis of coal and char.

Coal	Coal conversion 100 X X_{coal} (120)	Ultimate analysis (% daf)				
		C	H	N	S	O(diff.)
Shin-Yubari	0	87	5.6	1.9	0.3	5
	46	90	1.7	1.7	0.2	6
	60	90	1.4	1.5	0.3	7
	83	91	1.3	1.0	0.4	6
Taiheiyo	0	77	6.3	1.5	0.3	15
	74	90	2.3	1.3	0.0	7
	76	91	1.8	1.0	0.1	6
	93	92	1.9	1.0	0.1	5

oxygen containing surface complexes⁽⁵⁾. This seems to be a reason why the oxygen content in Shin-Yubari char increased after devolatilization, although the accuracy of the oxygen analysis is not enough to discuss more deeply.

The size of residual char was measured. Shin-Yubari coal agglomerated into one large cylindrical lump. The relationship between the volume of the lump and the conversion was determined. The volume calculated on the assumption of unreacted core model shows a fairly good correlation with the observed volume. Taiheiyo coal is a non-caking coal, and the average size of residual char was determined by sieving. The calculated particle size on the same assumption as above was smaller than the observed value. The gasification might take place more homogeneously in the particle. A larger ash content in Taiheiyo coal also might prevent a quick shrinkage of particle.

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