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Hydropyrolysis of coal in a pressurized powder-particle fluidized bed using several catalysts

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Abstract

A sub-bituminous coal was pyrolyzed in hydrogen in a pressurized powder-particle fluidized bed. The coal powder was continuously fed into the bed, in which catalyst particles were fluidized. The effects of $CoMo/Al_2O_3$ and several types of zeolite catalysts on the product yields were examined. In the presence of catalysts, a high yield of hydrocarbon liquid was obtained. The main components were light aromatic hydrocarbons such as BTX and naphthalene. The product yields strongly depended on the gas atmosphere, catalyst type, pyrolysis temperature and pyrolysis pressure. Maximum yields of light aromatic hydrocarbons, 10.9 wt% (8.1 wt% of BTX and 2.8 wt% of naphthalene and cresol) were achieved using MS-13X catalyst at the pyrolysis conditions of 730°C and 1.0 MPa of hydrogen. The methane yield of 52 wt% was obtained with $CoMo/Al_2O_3$ catalyst at 730°C. The char produced in this process showed large reactivity for CO_2 gasification. © 1997 Elsevier Science B.V.

Keywords: Coal; Hydropyrolysis; Catalyst; Fluidized bed; Pressure

1. Introduction

Coal has been utilized as fuels, chemicals and reducing agents via combustion, gasification, liquefaction and carbonization processes. Hydropyrolysis of coal produces a liquid as chemical feed stock and as motor fuel, a high BTU gas and a char. An integrated process coupling hydropyrolysis and gasification/combustion of the residual char is one of the most attractive routes for coal conversion. In order to develop and commercialize a hydropyrolysis process, it is very important to obtain high yields of hydrocarbon liquids such as benzene, toluene and xylene (BTX). Use of a catalyst in a hydropyrolysis process is a possible way of controlling the final product distribution and obtaining high yields of light aromatic hydrocarbons selectively [1–5]. Several studies [3,6,7] on the hydropyrolysis of catalyst-loaded coals were performed. Maa et al. [3] carried out the hydropyrolysis of Mo-impregnated sub-bituminous coal at 7 MPa in a fixed-bed reactor and reported that catalytic two-stage hydropyrolysis doubled liquid yields from non-catalytic hydropyrolysis. Yamashita et al. [6] found out that the BTX yield was increased by the addition of Fe or Ni and 2.0 wt% of BTX yield was obtained with Fe-impregnated brown coal at a hydrogen pressure of 5 MPa. In the development of a catalytic coal hydropyrolysis process, the separation of catalyst from residual char is one of the big problems [8]. It seems that the recovery of catalyst

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from catalyst-loaded coal char or ash is practically difficult. Many studies [5,6,9–11] have been carried out using a two-stage reactor for the hydrotreatment of volatile matter from coal. Nelson and Tyler [9] investigated the catalytic upgrading of volatile matter from a sub-bituminous coal using a two-stage reactor and obtained 3.2 wt% of BTX with $NiMo/Al_2O_3$ catalyst in atmospheric hydrogen. Xu et al. [5] reported 2.6 wt% of BTX yield with Ni/W catalyst at atmospheric hydrogen pressure.

The final product distribution from catalytic coal pyrolysis is determined by the primary reactions of the coal and subsequent secondary reactions of the primary products. The secondary reaction of volatile matter occurs mainly in the gas phase and on the catalyst surface. The authors have been developing a coal pyrolysis process using a powder-particle fluidized bed (PPFB) [12,13]. The PPFB system has been devised for the processing of fine powder [14,15]. Fine coal powder fed into a bed in which large catalyst particles are fluidized is rapidly pyrolyzed, and secondary reactions of volatile matter occur simultaneously. In this system, an immediate hydrocracking of the heavy hydrocarbons produced from coal is realized in the fluidized bed of catalyst. In the PPFB system, the residual char entrained from the bed is recovered by a cyclone or a bag filter. Thus, char is easily separated from catalyst. This system is very similar to that used by Tyler [16,17]. Tyler and Nelson [1] examined the effects of CoMo and NiMo catalysts as fluidizing particles on the product composition, and reported a high yield of light oil in a hydrogen atmosphere. In spite of many studies on fluidized-bed pyrolysis [1,8,16,17,21] limited information on the effect of catalysts on the yields of BTX is available. In a previous study [13], Taiheiyo sub-bituminous coal was pyrolyzed in hydrogen in a PPFB at atmospheric pressure. In the presence of $CoMo/Al_2O_3$, a hydrocarbon liquid with a narrow product distribution was recovered. The product distribution was quite sensitive to the pyrolysis temperature; maximum yields of light aromatic hydrocarbons, 7.2 wt% (BTX 5.8 wt%, naphthalene 1.4 wt%), ~30 times those with silica sand, were obtained at 590°C.

The yields and quality of the products were affected by many operating parameters: temperature, pressure, reactor type, residence time, heating rate, etc. In particular, in the case of hydropyrolysis using catalysts, the yields of light hydrocarbon liquids strongly depend on pyrolysis pressure [10,18,19]. The BTX yields of 10.4 and 14.0 wt% were reported using $NiMo/Al_2O_3$ [10] and USY-zeolite [11] under a hydrogen pressure of 5 MPa, respectively. In many previous studies, however, a small amount of coal was processed in a batch reactor. From a practical point of view, a continuous operation is desirable to evaluate the performance of hydropyrolysis system.

In this study, coal is continuously pyrolyzed in a pressurized PPFB under a hydrogen pressure of 1.0 MPa in order to obtain high BTX yield. $CoMo/Al_2O_3$ and several zeolite catalysts were selected as the fluidizing particles. The effects of the operating conditions on the yields of gases and light aromatic hydrocarbons were examined. The characteristics of chars recovered such as the ultimate analysis, the proximate analysis and the CO_2 gasification reactivity, were investigated.

2. Experimental

2.1. Materials

Taiheiyo coal (Japanese sub-bituminous coal) was used. The coal was crushed and sieved to 45–74 μm. Table 1 shows the proximate and ultimate analyses of the coal. Presulfided $CoMo/Al_2O_3$ catalyst (Co 2.6, Mo 9.0, S 0.5 wt%; C20-6, Catalysts and Chemicals,

Table 1
Analysis of Taiheiyo coal

Proximate analysis (wt%)				Ultimate analysis (wt%, daf)				
Moisture	VM	Ash	FC	C	H	N	S	$O_{diff.}$
5.3	45.7	11.2	37.8	77.9	6.4	1.3	0.3	14.4

Far East), Molecular Sieve 13X (Na_{86} $[(AlO_2)_{86}$-$(SiO_2)_{106}]_{276}H_2O$; MS-13X, Wako Pure Chemical Industries), USY-zeolite (SiO_2 78.3, Al_2O_3 21.5, Na_2O 0.28 wt%; HSZ-330HUD, TOSOH), HY-zeolite (SiO_2 73.2, Al_2O_3 22.3, Na_2O 4.3 wt%; HSZ-320HOD, TOSOH), NaY-zeolite (SiO_2 67.2, Al_2O_3 20.4, Na_2O 12.5 wt%; HSZ-320NAD, TOSOH), H-Mordenite (SiO_2 89.7, Al_2O_3 9.72, Na_2O 0.44 wt%; HSZ-620HOD, TOSOH) and Na-Mordenite (SiO_2 86.0, Al_2O_3 7.7, Na_2O 5.0 wt%; HSZ-620HOD, TOSOH) were used as fluidizing particles. Acidity of the zeolite catalysts was evaluated by calorimeter method measuring the differential heat of adsorption of ammonia. Silica sand was selected as a reference material. These particles were sieved to 250–500 μm and fluidized to eliminate fine particles stuck prior to pyrolysis runs for about 1 h. No chemical pretreatments of all the catalysts were conducted.

2.2. *Apparatus and procedure*

2.2.1. *Pyrolysis*

Fig. 1 shows a schematic diagram of the experimental apparatus. The main components of the pressurized fluidized-bed system were a coal feeder, fluidized-bed reactor, cyclone, gas bag and cold trap. The coal feeder was similar to that described elsewhere [13]. The reactor made of Inconel, 30 mm i.d. and 850 mm long was heated electrically. The cold trap comprised three Inconel tubes connected in series. The pyrolysis temperature was measured with a chromel–alumel thermocouple immersed in the fluidized bed. After the pyrolysis system had been fully purged and then pressurized with nitrogen, the catalyst particles in the reactor were fluidized at the desired flow rate and the temperature was raised to the desired level. Then the nitrogen was replaced by hydrogen or helium. When steady conditions had been established, dried coal was continuously fed at ~10 g/h into the fluidized bed, typically for ~1 h. The amount of catalyst loaded was about 50 g. Char particles elutriated from the bed were collected by the cyclone. Of the effluent gas from the reactor, about 8 l/min was introduced into a cold trap at ~−80°C and the remainder was caused to flow to a gas sampling system. About 2 l of the gas was collected by a gas bag at intervals of 10 min. The yields of gases (CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, CO_2, CO), BTX, phenol, cresol and naphthalene were determined with a gas chromatograph (GC). The condensable hydrocarbons collected in the cold trap and the tar adhering to the surfaces of the stainless steel tubes were dissolved with THF and the solution was examined by GC–MS. A capillary column (HiCap-CBP1, 0.2 mm i.d.×50 m) was used for separation, programmed at 40°C for 2 min and then at 4 K/min to 270°C.

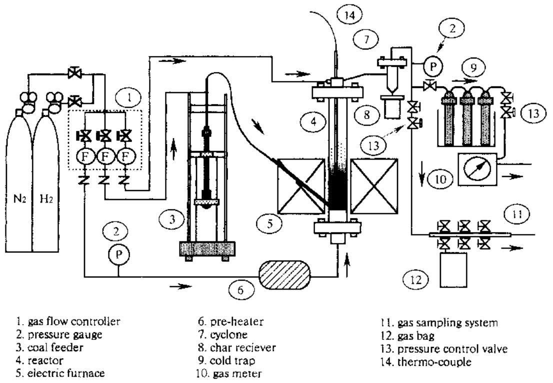

Fig. 1. Schematic diagram of experimental apparatus.

The weights of chars remained in the fluidized-bed reactor, cyclone and all stainless steel tubes were measured to establish the mass balance in each experiment. Water and tar trapped in the cold trap were not measured, but the total weight of the char recovered and the weight of the products determined with a GC amounted to 85–105 wt% of the coal feed. The mass balance in these experiments was fairly complete. About 0.5 wt% of catalyst loaded in the reactor was elutriated from the bed during the pyrolysis experiment. This is one of the disadvantages of the fluidized-bed system.

The ranges of experimental conditions were as follows: pyrolysis temperature 510–735°C; static bed height 10–13 cm; gas flow rate 16–27 l/min; gas residence time in fluidized bed 0.7–0.8 s; pyrolysis atmosphere hydrogen or nitrogen.

Product yields are expressed on the dry, ash-free coal basis.

2.2.2. *CO_2 gasification*

CO_2 gasification was conducted in a thermobalance (Shinku-Riko TGD-7000RH). The sample was heated to gasification temperature at the rate of 500 K/min in nitrogen atmosphere. Then carbon dioxide of 0.1 MPa was introduced and gasification reaction was initiated. Gasification was allowed to continue for 2 h. The gasification temperature was 750°C. The remaining char was completely burnt with oxygen (burning time 10–30 min), and the total amount of ash in the sample was checked for each experiment.

3. Results and discussion

3.1. *CoMo/Al_2O_3 catalyst as fluidizing particles*

3.1.1. *Effect of atmosphere*

Pyrolysis of Taiheiyo coal was carried out in hydrogen and helium at a pressure of 1.0 MPa, using CoMo/Al_2O_3 catalyst as fluidizing particles. The pyrolysis temperature and the static bed height of catalyst particles were 580°C and 13 cm, respectively. Hydrogen gas feed rate was 25 l/min. The average gas residence time in the fluidized bed was about 0.7 s. The yields of light aromatic hydrocarbons were shown in Fig. 2. The yields strongly depended on the pyrolysis atmosphere. The light aromatic hydrocarbon yield in hydrogen was about four times than that in helium. The phenomenon observed in this study was quite similar to that observed in the hydropyrolysis experiment at atmospheric pressure. Thus, the CoMo/Al_2O_3–H_2 system in the PPFB was effective for obtaining high yields of light aromatic hydrocarbons not only at atmospheric pressure but also at the higher pressure of 1.0 MPa. The results obtained using an atmospheric PPFB in previous work [13] were also shown in Fig. 2. The yields of light aromatic hydrocarbons depended on the pyrolysis pressure and the yields at a hydrogen pressure of 1.0 MPa were considerably lower than those at 0.1 MPa. The yields of methane, the main product gas at 1.0 and 0.1 MPa were 32 and 6 (wt%, daf), respectively. This is due to the intensive progress of hydrocracking reactions of hydrocarbons released during the devolatilization of coal under a hydrogen pressure of 1.0 MPa.

3.1.2. *Effect of temperature*

Fig. 3 shows the effect of pyrolysis temperature on the yields of light aromatic hydrocarbons and methane for the hydropyrolysis of Taiheiyo coal at 1.0 MPa using CoMo/Al_2O_3 catalyst. The average gas residence time was kept at 0.7 s by controlling the flow rate at each temperature. The results obtained at 0.1 MPa in previous study [13] were also shown in Fig. 3. The product distribution was quite sensitive to the pyrolysis temperature. The yields of light aromatic hydrocarbons at 1.0 MPa increased with temperature up to 530°C and sharply decreased above 540°C. The results suggested that precise regulation of the

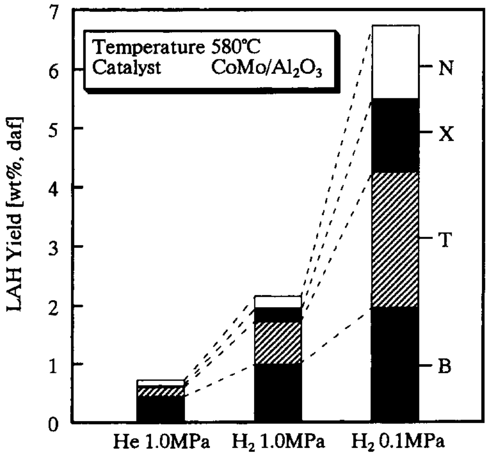

Fig. 2. Effect of pyrolysis condition on light aromatic hydrocarbon yields: B, Benzene; T, toluene; X, xylenes; and N, naphthalene.

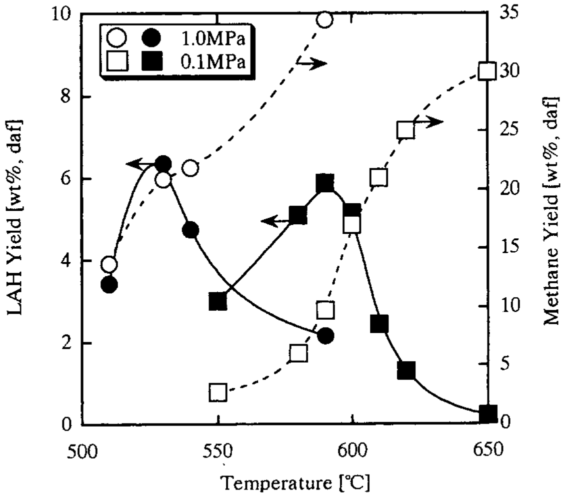

Fig. 3. Effects of pyrolysis temperature and hydrogen pressure on light aromatic hydrocarbon yield and methane yield: Catalyst, CoMo/Al_2O_3.

pyrolysis temperature is very important for the control of product distribution when using a catalyst not only at atmospheric hydrogen pressure but also at high hydrogen pressure. The fluidized-bed pyrolyzer is suitable from this point of view, because it is easy to achieve uniform control of the temperature in the catalyst bed. The methane yield increased with temperature and reached 32 wt% at 590°C. Maximum yields of light aromatic hydrocarbons were obtained at 530°C under a hydrogen pressure of 1.0 MPa and were almost identical to those obtained at 590°C under atmospheric hydrogen pressure. It was found that high yields of light aromatic hydrocarbons were achieved at moderate pyrolysis temperature of 530°C in the pressurized PPFB.

In the presence of CoMo/Al_2O_3, BTX, naphthalene, phenanthrene and pyrene were detected, and other hydrocarbons were negligible. The main components at 580°C were BTX and naphthalene, and phenanthrene and pyrene were formed significantly at 530°C.

The CoMo/Al_2O_3 catalyst was characterized after pyrolysis. The sulfur content decreased from 0.5 to 0.3 wt%, whereas the carbon content increased to 0.3 wt%, showing carbon deposition on the catalyst. The XRD pattern of the used catalyst was almost the same as that of the fresh one. This means that the crystal structure is almost unchanged. The specific surface area slightly decreased from the initial 233 to 216 m^2/g.

Seven succesive runs using the same catalyst were conducted at 530°C and 1.0 MPa to investigate the life of CoMo/Al_2O_3 catalysts. The amount of the catalyst used was 50 g and the amount of coal fed was about 8 g in every experiment. Fig. 4 shows the changes in product yields during succesive runs. The yields of hydrocarbon gases and liquids gradually decreased with an increase in the accumulative amount of coal fed and were finally 75% and 50% of those at the first run, respectively. The deactivation of CoMo/Al_2O_3 catalyst is in part due to the carbon deposition mentioned above.

3.2. *Zeolite catalysts as fluidizing particles*

3.2.1. *Effect of pyrolysis pressure*

Pyrolysis of Taiheiyo coal was carried out in hydrogen at 0.1 and 1.0 MPa, using MS-13X catalyst as fluidizing particles. The pyrolysis temperature and the static bed height of catalyst particles were 735°C and 10 cm. Hydrogen gas feed rate was 16 l/min. The average gas residence time was about 0.8 s. The yields of hydrocarbon gases and light aromatic hydrocarbons are shown in Figs. 5 and 6, respectively. The yields strongly depended on the pyrolysis pressure and increased with an increase in hydrogen pressure. The yields of gases and light aromatic hydrocarbons at 1.0 MPa were 2.4 and 2.2 times than that at 0.1 MPa, respectively. It is noteworthy that the yields of saturated hydrocarbon gases and unsubstituted aromatic hydrocarbons such as benzene and naphthalene were remarkably enhanced. The yields of light aromatic hydrocarbons obtained using MS-13X were

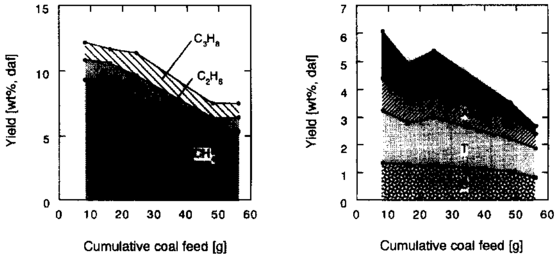

Fig. 4. Variation of product yields during seven successive runs: Catalyst, CoMo/Al_2O_3; H_2, 1.0 MPa, and temperature, 735°C; keys as in Fig. 2.

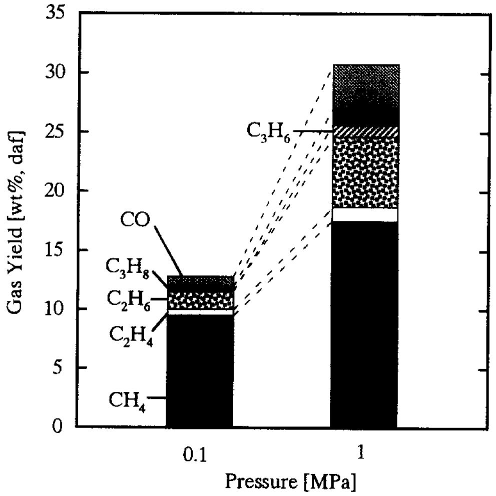

Fig. 5. Effect of pyrolysis pressure on product gas yields: Catalyst, MS-13X; and temperature, 735°C.

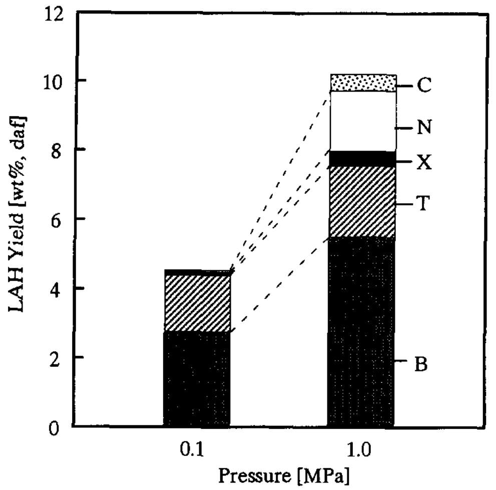

Fig. 6. Effect of pyrolysis pressure on light aromatic hydrocarbon yields: Catalyst, MS-13X; temperature, 735°C; keys as in Fig. 2; and C, cresol.

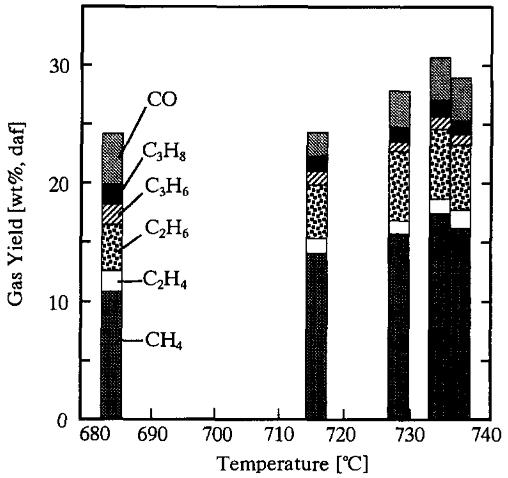

Fig. 7. Effect of pyrolysis temperature on product gas yields: Catalyst, MS-13X; and H_2, 1.0 MPa.

much higher than those using $CoMo/Al_2O_3$ shown in Fig. 3.

GC–MS data of condensable liquids produced at 1.0 MPa and 735°C revealed that, compared with the results obtained using $CoMo/Al_2O_3$, the hydropyrolysis with MS-13X was more selective for the production of light aromatic hydrocarbons. This is one of the important advantages of the pressurized PPFB system using MS-13X.

After pyrolysis, the carbon content of MS-13X increased to 0.8 wt%. The amount of the carbon deposited on the catalyst was larger than that on $CoMo/Al_2O_3$. This may be due to a higher pyrolysis temperature in the case of MS-13X. The XRD pattern of the catalyst was almost unchanged before and after pyrolysis. The specific surface area decreased from initial 547 to 499 m^2/g.

3.2.2. *Effect of pyrolysis temperature*

Figs. 7 and 8 show the effect of pyrolysis temperature on the product distributions for the pressurized hydropyrolysis of Taiheiyo coal using MS-13X catalyst at 1.0 MPa. The average gas residence time was kept at 0.8 s by controlling the flow rate at each temperature. The product distribution was relatively insensitive to the pyrolysis temperature, unlike the results using $CoMo/Al_2O_3$ catalyst. The gas yields of 24–31 wt% and the light aromatic hydrocarbon yields of 8.1–10.9 wt% were obtained at the temperature range among 685–740°C. Maximum light aromatic hydrocarbon yields of 10.9 wt% (8.1 wt% of BTX and 2.8 wt% of naphthalene and cresol) were obtained at 730°C. Krabiell et al. [19] investigated the influence of the CoMo catalyst on the BTX yield. The BTX yield was increased with an increase in hydrogen pressure up to 6.0 MPa and the BTX yields of 2.1 and 4.4 wt%

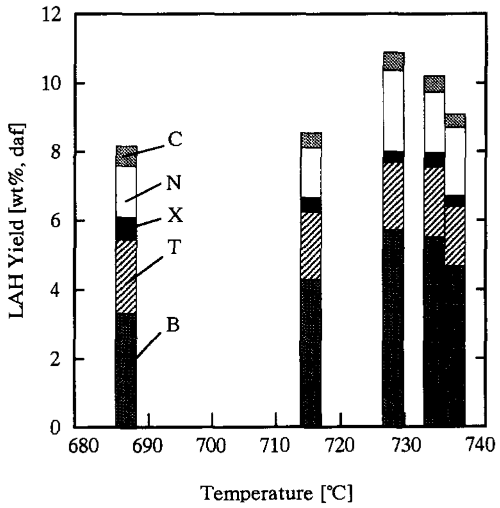

Fig. 8. Effect of pyrolysis temperature on light aromatic hydrocarbon yields: Catalyst, MS-13X; and H_2, 1.0 MPa; keys as in Fig. 6.

were reported at 1.0 and 6.0 MPa, respectively. The BTX yields of 10.4 and 14.0 wt% from the pyrolysis of Millmerran sub-bituminous coal were reported using NiMo/Al_2O_3 [10] and USY-zeolite [11] under a hydrogen pressure of 5 MPa, respectively. Suuberg et al. [20] obtained 5.3 wt% of light hydrocarbon liquid yield from the rapid hydropyrolysis of Pittsburgh Seam bituminous coal at a hydrogen pressure of 6.9 MPa. In this study, a higher yield of light aromatic hydrocarbons (10.9 wt%) was obtained at a pressure as low as 1.0 MPa. It appears that the pressurized PPFB with MS-13X catalyst is suitable for the production of such hydrocarbons under moderate pyrolysis conditions.

3.2.3. *Effect of zeolite type*

The effect of zeolite type on the product distribution was investigated under the hydropyrolysis conditions of 1.0 MPa and 730°C. The product yields obtained are shown in Figs. 9 and 10 together with those with silica and CoMo/Al_2O_3. The product gas yield slightly depended on the particle type, except for CoMo/Al_2O_3. With MS-13X and USY-zeolite, the product gas yields were relatively higher than those with the other zeolites. With CoMo/Al_2O_3, a higher methane yield of 52 wt% was observed, whereas the yields of light aromatic hydrocarbons were negligibly small.

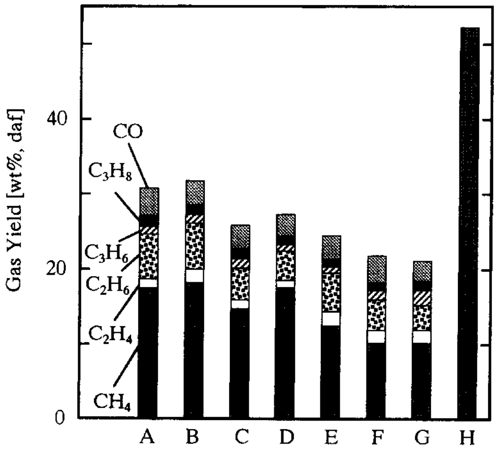

Fig. 9. Effects of zeolite catalysts on product gas yields: A, MS-13X; B, USY-zeolite; C, HY-zeolite; D, NaY-zeolite; E, H-Mordenite; F, Na-Mordenite; G, SiO_2; and H, CoMo/Al_2O_3; H_2, 1.0 MPa; and temperature, 730°C.

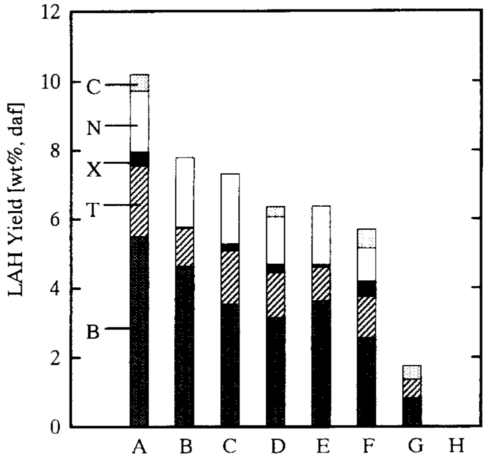

Fig. 10. Effects of zeolite catalysts on light aromatic hydrocarbon yields: H_2, 1.0 MPa; and temperature, 730°C; keys as in Figs. 6 and 9.

Almost all the hydrocarbons released were converted to methane with CoMo/Al_2O_3 catalyst. A part of methane evolved might be produced from the hydrogasification of the carbon deposited on the catalyst surface.

All the zeolite catalysts examined gave much higher yields of light aromatic hydrocarbons than silica sand. Among the zeolite catalysts, the activity sequence for the production of light aromatic hydrocarbons was MS-13X>Y-type zeolites>Mordenites, and MS-13X was thus most effective. On the other hand, the acidity sequence was H-Mordenite$\sim$USY$\gg$MS-13X. Thus, the yields of light aromatic hydrocarbons increased with a decrease in the acidity of catalyst. The distribution of benzene (B), toluene (T), and xylenes (X) strongly depended on the zeolite type. The yield ratios of B : T : X were 13 : 5 : 1, 45 : 12 : 1, and 97 : 23 : 1 with MS-13X, H-Mordenite, and USY, respectively. The product distribution also depended on the Na content of zeolite catalyst. The ratios of B : T : X were 45 : 12 : 1, 6 : 3 : 1, 21 : 8 : 1, and 12 : 5 : 1 with H-Mordenite, Na-Mordenite, HY, and NaY, respectively. Since it is generally accepted that the acidity of Na-loaded zeolite is lower than that of H-type one [22], the use of zeolites with lower acidity may result in higher yields of branched aromatics.

The pore size of the zeolite may be another factor for determining the product distribution. The pore sizes of MS-13X, Y-type zeolites and Mordenites were

1.1, 0.8 and 0.7 nm, respectively, and the yields of light aromatic hydrocarbons increased with an increase in the pore size. Chareonpanich et al. [11] examined the effects of USY-zeolite and MS-13X on the yields of light hydrocarbon liquids using a two-stage reactor at a hydrogen pressure of 5 MPa and reported that USY-zeolite was suitable for BTX production, whereas MS-13X was more suitable for the co-production of naphthalene. In this study, naphthalene was appreciably produced with USY-zeolite. This means that the product distribution strongly depends on the reactor type and the pyrolysis conditions. With Na-type zeolites, the production of cresol was observed.

3.3. Characteristics of char

3.3.1. Volatile matter in char

Fig. 11 shows the volatile matter of the char collected by the cyclone. The volatile matter was strongly dependent on the pyrolysis temperature and decreased monotonically with an increase in temperature. The char produced from the relatively low-temperature pyrolysis yields a significant amount of volatile matter. The char produced around 530°C still has 35 wt% volatile matter and its fuel ratio (fixed carbon/volatile matter) is 1.9. Such char can be utilized as a fuel. The volatile matter hardly depended at all on the kind of fluidizing particles. The type of the fluidizing particles is considered to have little effect on the primary pyrolysis of coal.

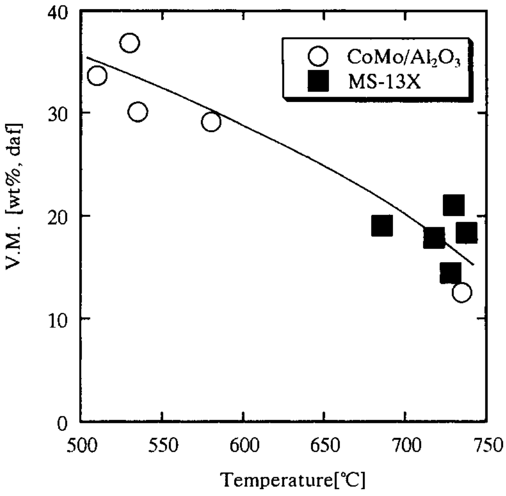

Fig. 11. Effect of temperature on volatile matter of char: H_2, 1.0 MPa.

3.3.2. Ultimate analysis of char

The ultimate analysis of the char collected in the cyclone was determined. The results are shown in Table 2. The elemental composition depended on the pyrolysis temperature. The H/C ratio of char decreased with an increase in pyrolysis temperature. Surprisingly, the O/C ratio of the char produced at around 530°C was almost identical to that of raw coal. This means that the conversions of carbon and oxygen are almost the same at a low temperature of 530°C. The elemental composition of char was independent

Table 2
Ultimate analysis of char produced in 1.0 MPa hydrogen

Temperature (°C)	Catalyst	Ultimate analysis (wt%, daf)				H/C	O/C
		C	H	N	$O_{diff.}$		
510	$CoMo/Al_2O_3$	75.7	5.3	1.7	17.3	0.84	0.17
530	$CoMo/Al_2O_3$	77.7	4.7	1.8	15.8	0.73	0.15
536	$CoMo/Al_2O_3$	78.3	4.5	1.8	15.0	0.69	0.14
580	$CoMo/Al_2O_3$	76.3	4.4	1.9	17.4	0.69	0.17
686	MS-13X	85.3	4.1	1.9	8.7	0.58	0.076
717	MS-13X	86.5	3.9	1.8	7.8	0.54	0.068
730	MS-13X	86.9	3.6	1.8	7.8	0.50	0.067
735	MS-13X	86.4	3.6	1.8	8.1	0.50	0.070
735	USY-zeolite	84.7	3.4	1.6	10.3	0.48	0.091
735	H-Mordenite	85.7	3.5	1.6	9.5	0.49	0.083
735	$CoMo/Al_2O_3$	87.8	3.4	2.0	6.8	0.46	0.058

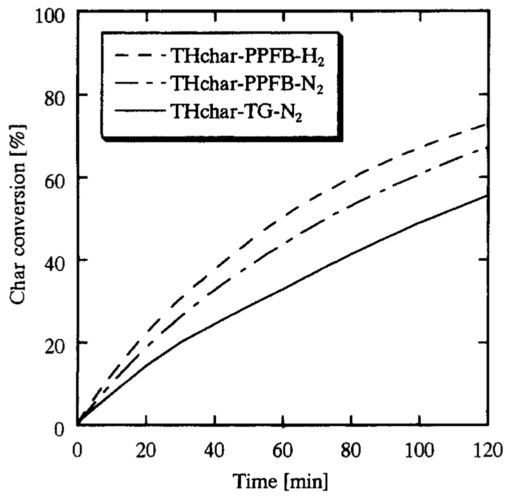

Fig. 12. CO_2 gasification profiles of chars prepared in PPFB and TG.

of the particle type. The result also suggests that the type of fluidizing particles has little effect on the primary pyrolysis of coal.

3.3.3. CO_2 *gasification reactivity*

The chars were prepared in PPFB in hydrogen and nitrogen at a pressure of 1.0 MPa and in TG in atmospheric nitrogen. CO_2 gasification was carried out in a thermobalance at 750°C. The reactivities of chars recovered from PPFB system and prepared in TG are shown in Fig. 12. The reactivity of char produced in nitrogen in the PPFB (THchar-PPFB-N_2) was higher than that of char prepared in TG (THchar-TG-N_2). Previous investigators reported that the reactivity of char depended on the heating rate, atmosphere and pressure in the pyrolysis stage [23,24]. CO_2 gasification rates of chars were increased with an increase in the heating rate [23,24]. The rapid pyrolysis in PPFB may be one of the reasons for high reactivity of char. The reactivity of char produced in hydrogen in the PPFB (THchar-PPFB-H_2) was much higher than that of THchar-PPFB-N_2. Matsui and Nakahori [23] reported that the steam gasification reactivity of char prepared in hydrogen atmosphere was higher than that of char prepared in helium atmosphere. It is thought that sites active towards gasification agents are formed during the devolatilization of coal in hydrogen atmosphere.

4. Conclusions

Coal was continuously pyrolyzed in a pressurized PPFB. The following conclusions were obtained.

1. The product distribution can be controlled by the pyrolysis temperature, the catalyst type and the hydrogen pressure.
2. Light aromatic hydrocarbons were produced selectively in the presence of catalysts.
3. Maximum yields of light aromatic hydrocarbons, 10.9 wt% (8.1 wt% of BTX and 2.8 wt% of naphthalene and cresol) were achieved using MS-13X catalyst at the hydropyrolysis conditions of 730°C and 1.0 MPa.
4. The pressurized PPFB produced chars with large reactivities towards CO_2 gasification.

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