

## CATALYTIC HYDROCRACKING REACTION OF NASCENT COAL VOLATILE MATTER UNDER HIGH PRESSURE IN A TWO-STAGE REACTOR

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### INTRODUCTION

Various products are generated in coal pyrolysis. Usually, the yield of useful chemicals such as benzene, toluene, and xylenes (BTX) is low. If it can be increased to a considerable degree, a combination of flash pyrolysis of coal and gasification/combustion of residual char can become an efficient way to utilize coal. Coal pyrolysis consists of two steps. In the first step, radical species are generated and stabilized. In the second step, the secondary reaction of nascent products occurs in the char pore, in the gas-phase and/or on the char or catalyst surface. In our previous studies [1-4], the modification of the distribution of final products has been tried under the conditions where the primary reaction and the secondary reaction are separated as far as possible. From these studies, it was found that the product yield could be modified by controlling the secondary reaction in which the utilization of catalyst was quite effective.

Previous studies on the utilization of catalyst in coal pyrolysis can be classified into two types: i) hydrocracking of coal volatiles over catalysts added directly on coal [4-6], ii) hydrocracking of volatiles over catalysts placed separately from coal [3, 7, 8]. The results of these studies suggested that the yield of chemicals, such as BTX, can be increased by the following two factors: high  $H_2$  pressure and effective catalyst. However, the coal pyrolysis under high pressure with subsequent catalytic hydrocracking of nascent volatile has not been examined extensively.

In the present study, a two-stage reactor which can be operated under high pressure was made. Using this reactor, coal was pyrolyzed under high pressure of hydrogen in the first stage and the coal volatiles was hydrocracked over sulfided Mo-based catalyst in the second stage. In order to design the distribution of final products, the effects of gas pressure, catalyst, coal type, and reaction temperature on the coal pyrolysis and post-cracking have been clarified.

### EXPERIMENTAL

**Apparatus and procedure.** The schematic diagram of the two-stage reactor used in this study is shown in Fig. 1. The reactor is a SUS-316 tube (i.d. 7.6 mm).  $H_2$  or He at pressure of 0.1-5 MPa was used ( $200 \text{ ml(NTP) min}^{-1}$ ). A coal sample (10 mg) was placed in a small quartz boat and was pyrolyzed in the first-stage by heating with an infrared furnace at a rate of  $10 \text{ K s}^{-1}$  up to a temperature ( $T_1$ )

ranging 500-800°C and held there for 2 min. The evolved volatile matter was introduced into the second-stage where the catalyst (800 mg) was packed and the temperature ( $T_2$ ) was controlled at 400-700°C by another electric furnace. The final products were collected in a cold trap packed with Porapak P. After depressurization, the collected products were allowed to desorb from the trap and subjected to g.c. analysis.

**Coal sample and catalyst.** Five coals from Australia were used: one bituminous coal; Liddell (C, 83.5 % daf), two subbituminous coals; Wandoan (C, 78.5 %), Millmerran (C, 76.9 %) and two brown coals; Morwell (C, 67.4 %), Loy Yang (C, 66.7 %). Particle size of the coal sample was <100  $\mu\text{m}$ . The sample was dried in  $\text{N}_2$  at 107°C for 1 h before use. Ni/Mo/ $\text{Al}_2\text{O}_3$  (NiO: 2.8 wt%,  $\text{MoO}_3$ : 10.3 wt%) from Harshow and Co/Mo/ $\text{Al}_2\text{O}_3$  (CoO: 3.9 wt%,  $\text{MoO}_3$ : 10.8 wt%) from American Cyanamid were used as catalysts. Catalyst pellets were crushed to 32-60 mesh. Prior to each series of experiments, the catalyst was calcined in oxygen for 0.5 h, and treatment with hydrogen sulfide ( $\text{H}_2\text{S}$ , 4 %;  $\text{H}_2$ , balance) was carried out at 500°C for 0.5 h, followed by further treatment with hydrogen for 0.5 h. Ni/Mo/S and Co/Mo/S stand for the sulfided catalysts.

## RESULTS AND DISCUSSION

**Effect of gas pressure in the first-stage.** The effect of gas pressure on the coal pyrolysis in the first-stage was investigated without catalyst in the second-stage (Table 1). The amount of volatile (weight loss) increased with increasing pressure of  $\text{H}_2$  and with decreasing pressure of He. Hydrogen stabilizes the radical generated in the primary reaction, increasing the amount of volatile. The BTX yield increased with pressure in both gases. The increase of BTX yield observed in  $\text{H}_2$  was larger than that in He. The secondary reaction of volatiles in char pore might be responsible for the pressure effect observed in the inert atmosphere of He.

**Effect of catalyst and  $\text{H}_2$  pressure in the second-stage.** The effects of catalyst and  $\text{H}_2$  pressure on the distribution of final products were studied by using several catalysts. The results obtained using Liddell coal at the temperature of  $T_1=600^\circ\text{C}$  and  $T_2=500^\circ\text{C}$  are shown in Table 2.  $\text{Al}_2\text{O}_3$  was not effective to increase BTX yield which was similar to that without catalyst under a high  $\text{H}_2$  pressure. On the other hand, Co/Mo/S and Ni/Mo/S catalysts were effective for the secondary reaction even under atmospheric pressure. A high pressure remarkably increased the yields of BTX and hydrocarbons, especially the yield of benzene and methane. Ni/Mo/S catalyst was more effective.

**Effect of reaction temperature.** Effect of reaction temperature of the first- or the second-stage was investigated with Millmerran coal, Ni/Mo/S, and 5 MPa  $\text{H}_2$  (Table 3). With a constant  $T_2$  of 500°C, the BTX yield increased with increasing  $T_1$ . On the other hand, at  $T_1$  of 600°C, the maximum yields for BTX and hydrocarbon were obtained at a moderate  $T_2$  (600°C). Using the two-stage reactor, the optimum temperatures for the first- and the second-stage can be selected independently.

**Effect of coal types.** Effect of coal type on the yield of final products is shown in Table 4. For all the coals, the amount of volatiles increased with H<sub>2</sub> pressure. However, the product distribution pattern was different among coals. Under high H<sub>2</sub> pressure, the highest BTX yield (6.2 %) were observed with Millmerran coal, while the highest C<sub>2</sub>-C<sub>7</sub> yield (17.1 %) were obtained with Wandoan coal. The present BTX yields were compared with those obtained using Curie-point pyrolyzer (CPP) under atmospheric pressure of argon without catalyst [1] (Fig. 2). The two-stage reaction with Ni/Mo/S catalyst leads to a large increase in BTX yield. The values obtained under atmospheric pressure were twice and those obtained under high pressure were five times larger than those obtained with CPP. A higher BTX yield was obtained by using coal with higher H/C ratio. This is because the coal with higher H/C ratio generates a larger amount of tar during the primary pyrolysis [1], and BTX is produced by the secondary reaction (hydrocracking) of primary tar over catalyst. It can be concluded that the secondary reaction over Ni/Mo/S catalyst under high H<sub>2</sub> pressure is effective for producing valuable materials.

## CONCLUSION

The yield of useful chemicals could be increased to a considerable extent by using catalyst under high H<sub>2</sub> pressure in a two-stage reactor. Coal with higher H/C ratio and operation under higher H<sub>2</sub> pressure are preferable for a high BTX yield. The type of catalyst is also an important factor. The Ni/Mo/S catalyst is the most effective. The higher reaction temperature in the first-stage was preferable and the moderate temperature of the second-stage was suitable for a high BTX yield. In the present study, the highest BTX yield (7.6 %) was observed under the following conditions: Millmerran coal, Ni/Mo/S catalyst, T<sub>1</sub>=800°C, T<sub>2</sub>=500°C, 5 MPa of H<sub>2</sub>

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**Table 1** Effect of Gas Pressure on Coal Pyrolysis.

Gas	Press. (MPa)	Weight loss (%, daf)	Yield (% daf)					
			CO <sub>x</sub>	CH <sub>4</sub>	C <sub>2</sub> -C <sub>7</sub>	BTX	PCX	Tar
He	0.1	34	5.4	2.4	2.4	0.6	0.9	22.3
	2.0	30	4.6	3.3	3.4	1.0	0.5	17.2
	5.0	28	6.4	3.3	3.2	1.0	0.6	13.5
H <sub>2</sub>	0.1	34	4.3	2.7	3.4	0.7	0.8	22.1
	2.0	36	4.7	5.2	3.8	2.1	0.7	19.5
	5.0	39	8.3	7.2	5.6	3.2	0.8	13.9

T<sub>1</sub>-T<sub>2</sub>: 600-500°C. Coal: Liddell. Catalyst: None.

**Table 2** Effect of Catalyst and H<sub>2</sub> Pressure on Product Yields from Secondary Reaction of Volatiles.

Catalyst	H <sub>2</sub> press. (MPa)	Yield (% daf)				
		CO <sub>x</sub>	CH <sub>4</sub>	C <sub>2</sub> -C <sub>7</sub>	BTX	PCX
None	0.1	4.3	2.7	3.3	0.7	0.8
	5.0	8.3	7.2	5.6	3.2	0.8
Al <sub>2</sub> O <sub>3</sub>	0.1	11.3	1.8	3.7	0.7	0.9
	5.0	10.2	5.0	11.3	2.9	0.9
Co/Mo/S	0.1	7.5	1.7	2.6	2.1	0.8
	5.0	2.0	4.4	7.4	4.7	0.8
Ni/Mo/S	0.1	4.3	4.4	4.3	2.1	0.9
	5.0	0.7	10.8	10.9	5.1	0.8

T<sub>1</sub>-T<sub>2</sub>: 600-500°C. Coal: Liddell.

**Table 3** Effect of  $T_1$  and  $T_2$  on Product Yields from Secondary Reaction of Volatiles.

$T_1$ - $T_2$ (°C)	Weight loss (%, daf)	Yield (% daf)			
		CH <sub>4</sub>	C <sub>2</sub> -C <sub>7</sub>	BTX	PCX
500-500	40	5.5	11.6	3.9	0.9
600-500	57	12.4	15.2	6.2	0.9
700-500	60	18.8	18.6	7.0	2.2
800-500	66	18.8	8.3	7.6	1.5
600-400	57	11.0	11.9	5.5	1.5
600-500	57	12.4	15.2	6.2	0.9
600-600	57	16.4	21.6	7.0	0.4
600-700	57	36.4	0.7	4.5	0.1

Catalyst: Ni/Mo/S. Coal: Millmerran.

**Table 4** Effect of Coal Types and H<sub>2</sub> Pressure on Product Yields from Secondary Reaction of Volatiles.

Coal	H <sub>2</sub> press. (MPa)	Weight loss (%, daf)	Yield (% daf)					
			CO <sub>x</sub>	CH <sub>4</sub>	C <sub>2</sub> -C <sub>7</sub>	BTX	PCX	Tar
Liddell	0.1	36	4.3	4.4	4.3	2.1	0.9	20.0
	5.0	42	0.7	10.8	10.9	5.1	0.8	13.7
Wandoan	0.1	46	8.8	4.5	6.7	2.5	1.1	22.4
	5.0	56	3.3	13.8	17.1	5.1	1.1	15.6
Millmerran	0.1	53	5.8	4.8	7.4	3.0	1.3	30.7
	5.0	57	1.2	12.4	15.2	6.2	0.9	21.1
Morwell	0.1	50	24.7	3.5	4.8	2.1	1.0	13.9
	5.0	64	2.3	11.4	9.9	5.2	0.8	34.4
Loy Yang	0.1	48	27.1	2.7	3.2	2.0	0.7	12.3
	5.0	56	3.7	14.7	10.8	3.4	0.6	22.8

$T_1$ - $T_2$ : 600-500°C. Catalyst: Ni/Mo/S.

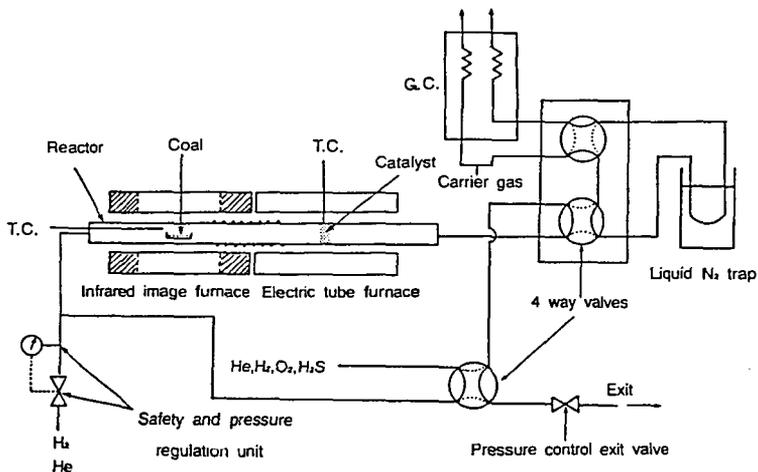


Fig. 1 Schematic diagram of a high pressure two-stage reactor.

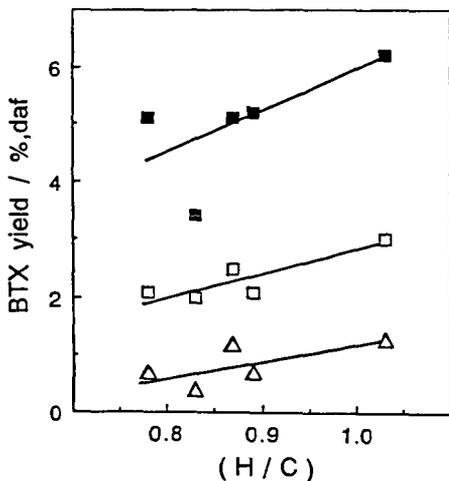


Fig. 2 Effect of H/C ratio of coal on BTX yields obtained in various reaction systems. (■) Two-stage reactor, Ni/Mo/S, 5 MPa H<sub>2</sub>; (□) two-stage reactor, Ni/Mo/S, 0.1 MPa H<sub>2</sub>; (△) CPP, none catalyst, 0.1 MPa Ar.