

# LIQUEFACTION OF INDONESIAN COALS WITH BOTTOM RECYCLE USING FeNi CATALYST SUPPORTED ON CARBON NANOPARTICLES

Unggul Priyanto<sup>1)</sup>, Kinya Sakanishi<sup>2)</sup>, Osamu Okuma<sup>3)</sup>, and  
Isao Mochida<sup>1)</sup>

1) Institute of Material Study, Kyushu University,  
Kasuga, Fukuoka 816-8580, Japan

2) National Institute for Resources and Environment,  
Tsukuba, Ibaraki 305-8569, Japan

3) The New Industry Research Organization, 1-5-2, Minatojima-minamimachi, Chuo-ku, Kobe  
650-0047, Japan

## Abstract

A series of coal liquefaction with bottom recycle was performed using FeNi catalyst supported on carbon nanoparticles (Ketjen Black: KB) at 450°C for single- and two-stage. In the single-stage, FeNi/KB catalyst gave excellent catalytic activity providing oil yield over 74% with successful reduction of catalytic loading to 0.15 wt% Fe and 0.15 wt% Ni d.a.f coal base.

Keywords: coal liquefaction; bottom recycle; iron nickel supported on KB

## Introduction

The main key of catalyst cost reduction for direct liquefaction of coal are recovery and repeated use of the catalyst. The major difficulty for the catalyst recovery comes from the mineral presence in coal. There are two approaches for catalyst recovery and regeneration. The first one is to eliminate or reduce the mineral in the coal, and another one is to design catalysts of ultrafine particle size and low specific gravity for recovery.<sup>1</sup>

Dow Chemical Co developed very small particles of molybdenum sulfide used as catalysts and were recovered and recycled with a novel hydroclone process.<sup>2</sup> The catalyst support can also provide such functions. The authors proposed a novel type of liquefaction catalyst with high activity and functions for recovery and repeated use.<sup>3-6</sup> NiMo and FeNi sulfides supported on particular carbon nanoparticles are catalysts, which can provide high distillate yields and can be separated from the solid residue by gravimetric separation for repeated use.

One of the major contributions for recycle of the catalyst or drastic reduction of its amount is to recycle non-distillate coal liquefaction products back to the initial stage of the process, which is termed as bottom recycle.<sup>7</sup> It has been recognized that large polycondensed aromatic rings from non-distillate products are very effective to disperse solvents for the very polar initial products of coal dissolution. Moreover, they can be hydrogenated easily to hydro aromatic structures, and have ability to shuttle hydrogen between unreacted coal, reacting molecules, and solvent components.<sup>8,9</sup>

In the present study, liquefaction of Tanito Harum and Adaro coals (Indonesian coals) was performed by using FeNi/KB catalyst to examine the effect of bottom recycle on the oil yield and the performance of H-donor (tetralin):

## Experimental Section

### Catalyst and Materials

A prescribed amount of Ketjen black was dispersed in methanol by ultrasonic irradiation for 15 min. Then, iron(II) fumarate and Ni(NO<sub>3</sub>)<sub>2</sub> dissolved in methanol were mixed to the KB-methanol slurry with a small amount of nitric acid (1% vol.) as an additive to prepare FeNi/KB catalyst. The slurry was dispersed by ultrasonic, and then, heated at 40°C for 2 h before the slurry was dried at 120°C for 12 h in vacuo. The catalyst was presulfided by flowing 5% vol H<sub>2</sub>S/H<sub>2</sub> at 360°C for 2 h prior to the reaction.

The elemental analysis of Tanito Harum coal is summarized in Table 1. Commercially guaranteed grade tetralin (TL) was used as liquefaction solvent.

### Liquefaction Procedure

Coal liquefaction was performed in an electromagnetic-driven autoclave of 50 ml capacity at 450°C for single stage, 380°C and 450°C for two-stage liquefaction.<sup>10</sup> Three grams of coal, 3 grams of solvent, and 0.09 grams of catalyst were charged to the autoclave.<sup>11</sup> The single- and two-stage liquefaction was performed under 15 MPa of hydrogen pressure. The heating rate to the reaction temperature was 20°C/min. The stirring speed was 1300 rpm. For two-stage liquefaction, the first stage was performed at 380°C for 15 min, and then the reactor was cooled down. Hydrogen gas was renewed after releasing out gaseous products. The second stage reaction was carried out at 450°C, 15 MPa for 105 min.

The liquefaction with repeated use of catalyst was done by recycling asphaltene, preasphaltene, residue, and used catalyst from run 1 to run 2 after they were separated from oil as illustrated in Figure 1. The liquefaction with bottom recycle was performed in 7 runs as illustrated in Figure 2. After the third run, a third of asphaltene, preasphaltene, residue, and used

catalyst was purged to prevent the accumulation of ash and unconverted materials. The remainder was recycled to the following run. To keep the the sulfidation state of the catalyst,  $\text{CS}_2$  was added in every run.<sup>12</sup>

The liquid and solid products of coal liquefaction were recovered with THF. After THF was removed by evaporation, the product was extracted in sequence with n-hexane, acetone, and THF. The n-hexane-soluble (HS), hexane-insoluble but acetone-soluble (HI-ACS), acetone-insoluble but THF-soluble (ACI-THFS), and THF-insoluble (THFI) substances were defined as oil(O) and solvent, asphaltene(A), preasphaltene(PA), and residue(R), respectively. The gas yield was calculated by weight difference between initial coal and recovered product. The oil yield was calculated by subtracting the solvent weight from the total weight of HS. The reaction under the same conditions was repeated at least three times to make sure the experimental result that were within 1wt% daf coal base.

## Results and Discussion

### Recycle of Heavy Residual Product and Repeated used of FeNi/KB catalyst

Table 1 describes results of residual product recycle in the single-stage liquefaction of Tanito Harum coal with FeNi/KB catalyst using process as illustrated in Figure 1. The liquefaction process in run 2 gave 69% oil yield that was comparable to that of run 1. It must be noted that there was no addition of fresh catalyst in run 2. It means that the activity of repeated use of FeNi/KB catalyst in run 2 was still high enough. Moreover, the oil yield was increased by hydrogenation of asphaltene and preasphaltene. The asphaltene, preasphaltene, and residue yields in the run 2 was average value of run 1 and 2.

### Effects of Reaction Procedure with Bottom Recycle Mode on the single-stage Liquefaction

Figure 3 describes effect of reaction process results in the single-stage liquefaction of Tanito Harum coal with FeNi/KB catalyst. The liquefaction yields from single run were showed in Figure 3a, and the yields from liquefaction with bottom recycle were showed in Figure 3b.

The liquefaction with heavy residual recycle was performed in 7 successive runs (see Figure 2). In the run 1 to 3, the liquefaction was done by utilizing bottoms recycle without purging to obtain the recycled catalyst/fresh catalyst ratio of 2. The liquefaction with bottom recycle provided average oil yield of 74%, which was 5% higher than that of liquefaction without bottom recycle. It is also be noted that the liquefaction only used fresh catalyst of 0.045 g each run compared to liquefaction without bottom recycle that used 0.09 g catalyst. It was suggested that high recycle ratio (recycled catalyst/fresh catalyst ratio) can improve significantly oil yields.

Table 3 shows liquefaction yields from liquefaction of Tanito Harum coal with bottom recycle each run. The lowest oil yields was obtained in the first run, which only carried the total catalyst of 0.045 g. In the second run, the oil yield highly improved in line with the addition of fresh catalyst. The highest improvement of oil yield occurred in this run followed by increasing gas yield reaching 18%. Large oil yield may be due to the conversion of asphaltene and preasphaltene sent from the first run.

The highest oil yield occurred in the third run. In this run, the total catalyst (fresh and used catalyst) reached 0.135 g. The highest oil yield in this run may be caused by a number of total catalyst that still had high activity and heavy residual products from previous runs. After the third run, the oil yield tended to decrease down to 74%, which showed the decrease of the catalyst activity. The oil yield appeared to be constant from the fifth run. In those run the activity of catalyst and a number of heavy residual products recycled become stationary.

Table 4 summarizes the conversion of tetralin into naphthalene after liquefaction of 60 min at 450°C, 15 MPa. Single-stage liquefaction with bottom recycle in the second run allowed 16% conversion that was much lower than that of liquefaction without bottom recycle (21% conversion), indicating that polynuclear aromatic ring of crude liquid bottom can aid in utilizing gaseous hydrogen. However, in the sixth run allowed 20% conversion inspite of higher total catalyst than that of the second run. This indicated the decrease of catalyst activity in the run.

### Effects of Reaction Procedure with Bottom Recycle Mode on the Two-stage Liquefaction

Figure 4 illustrates results of the two-stage liquefaction of Adaro coal with FeNi/KB catalyst. The liquefaction yields from single-stage, two-stage, and two-stage with bottom recycle was showed on Figures 4a, 4b, and 4c respectively. Single- and two-stage liquefaction of Adaro coal provided 68% and 80% oil yields respectively (see Figure 4a and 4b). The two-stage liquefaction with bottom recycle provided average oil yield of 82% that was 2% higher than that of liquefaction without bottom recycle. The combination of two-stage and bottom recycle gave very high oil yield.

Table 5 summarizes gas and oil yields from two-stage liquefaction of Adaro coal with bottom recycle in several runs. The highest oil yield occurred in the third run. After the fifth run, the oil yield tended to be constant.

## Conclusions

The liquefaction of coal with bottom recycle mode in the present study successfully improved oil yield, hydrogen transfer efficiently, and reduction of catalyst amount required. In this procedure, FeNi catalyst supported on carbon nanoparticles showed an excellent catalytic activity in the liquefaction with bottom recycle mode that can keep its activity in the repeated use.

## References

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**Table 1 Elemental Analyses of Coals Used in The Present Study**

	C <sup>a</sup>	H <sup>a</sup>	N <sup>a</sup>	O <sup>a</sup>	S <sup>a</sup>	Ash <sup>b</sup>	H/C
Adaro Coal	66.6	5.3	0.9	26.7	0.44	3.0	0.96
Tanito Harum Coal	71.2	5.5	1.6	21.7	0.16	3.9	0.93

<sup>a</sup> in Wt % (d.a.f.)

<sup>b</sup> in Wt. %

**Table 2 Liquefaction yields from Single-stage Liquefaction of Tanito Harum Coal with Repeated used Catalyst**

Run	Total catalyst g	Gas Yield Wt %	Oil yield Wt %	Asp <sup>a</sup> Wt %	Preasp <sup>a</sup> Wt %	Residue <sup>a</sup> Wt %
1	0.09	15	69	-	-	-
2	0.09	15	69	10	5	1

<sup>a</sup> average value of run 1 and 2

**Table 3 Liquefaction yields from Single-stage Liquefaction of Tanito Harum Coal with Bottom Recycle**

Run	Total catalyst g	Gas Yield Wt % (d.a.f)	Oil yield Wt % (d.a.f)	Asp Wt % (d.a.f)	Preasp Wt % (d.a.f)	Residue Wt % (d.a.f)
1	0.045	14 <sup>b</sup>	67 <sup>b</sup>	-	-	-
2	0.09	18 <sup>b</sup>	75 <sup>b</sup>	-	-	-
3	0.135	16 <sup>b</sup>	77 <sup>b</sup>	7 <sup>a</sup>	3 <sup>a</sup>	1 <sup>a</sup>
4	0.135	15 <sup>b</sup>	76 <sup>b</sup>	7 <sup>b</sup>	2 <sup>b</sup>	1 <sup>b</sup>
5	0.135	15 <sup>b</sup>	74 <sup>b</sup>	10 <sup>b</sup>	1 <sup>b</sup>	1 <sup>b</sup>
6	0.135	15 <sup>b</sup>	74 <sup>b</sup>	9 <sup>b</sup>	2 <sup>b</sup>	1 <sup>b</sup>
7	0.135	15 <sup>b</sup>	74 <sup>b</sup>	9 <sup>b</sup>	2 <sup>b</sup>	1 <sup>b</sup>

<sup>a</sup> average value of run 1, 2, and 3

<sup>b</sup> relative value of each run based on its coal feed

**Table 4 Conversion of Tetralin during Coal Liquefaction <sup>a</sup>**

Reaction Process	Total Catalyst g	Tetralin Conv (%)
Single-stage	0.09	21
Single-stage with bottom recycle <sup>b</sup>	0.09	16
Single-stage with bottom recycle <sup>c</sup>	0.135	20

<sup>a</sup> Reaction Condition : 450°C, 60 min, 15 MPa; stirring speed : 1300 rpm.

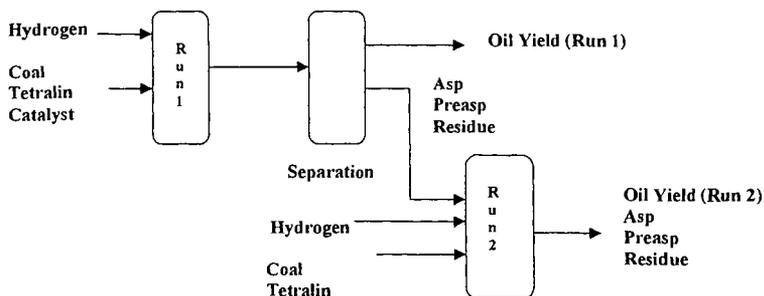
<sup>b</sup> in the second run (see table 3)

<sup>c</sup> in the sixth run

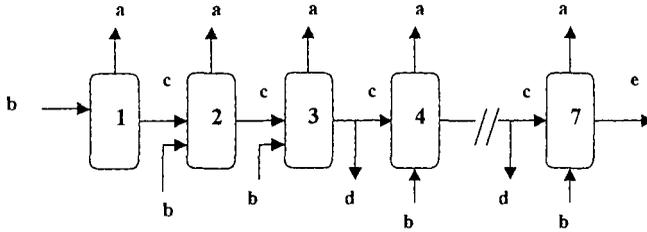
**Table 5 Gas and Oil Yields from Two-stage Liquefaction of Adaro Coal with Bottom Recycle**

Run	Total Catalyst g	Gas Yield <sup>a</sup> Wt %	Oil Yield <sup>a</sup> Wt %
1	0.045	13	74
2	0.09	19	84
3	0.135	14	87
4	0.135	14	85
5	0.135	14	85
6	0.135	15	81
7	0.135	15	81

<sup>a</sup> relative value of each run based on its coal feed



**Figure 1 Coal liquefaction process in series**



- a Oil Yield
- b Feed of coal(3 g), tetralin(3 g), and catalyst(0.045)
- c Yields of Asphaltene, preasphaltene, reused catalyst, and residue
- d Purge of asphaltene, preasphaltene, used catalyst, and residue
- e Last output of oil, asphaltene, preasphaltene, and residue

Figure 2. Liquefaction Process with Bottom Recycle

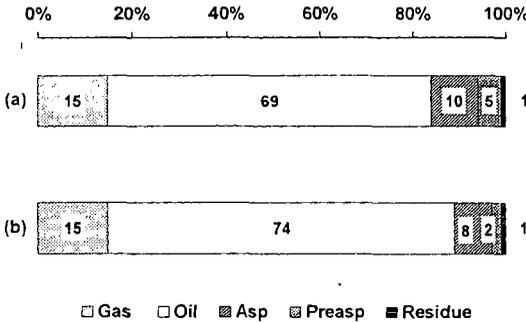


Figure 3. Effects of reaction process in the single-stage liquefaction of Tanito Harum coal with FeNi/KB catalyst, reaction conditions: 450°C, 15 MPa. Reaction processes: (a) Single stage at 60 min (b) Single-stage with bottom recycle performed for 60 min as given on Fig.2. For (a) coal/solvent/catalyst = (3 g)/(3 g)/(0.09g) and (b), coal/solvent/catalyst = (3 g)/(3 g)/(0.045 g)

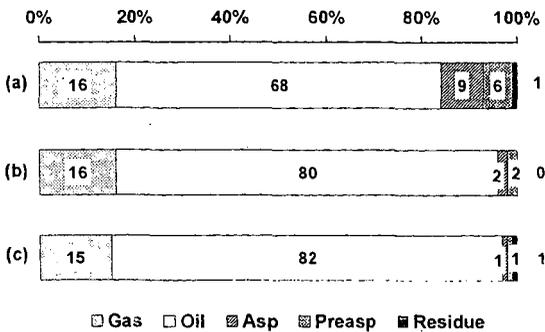


Figure 4. Effects of reaction process in the single- and two-stage liquefaction of Tanito Harum coal with FeNi/KB, Reaction Process: (a) is single-stage, and (b) is two-stage while (c) is two-stage with bottom recycle as given by Figure 2. Reaction times: (a) single-stage at 60 min; (b) 15 min at the first stage and 105 min at the second stage; (c) 15 min at the first stage and 105 min at the second stage each run. For (a) and (b), coal/solvent/catalyst = (3 g)/(3 g)/(0.09 g); For (c), coal/solvent/catalyst = (3 g)/(3 g)/(0.045 g).